(12) **EUROPEAN PATENT APPLICATION**

(54) Process for producing high tenacity, high modulus crystalline thermoplastic article and novel product fibers.

(57) Solutions of ultrahigh molecular weigh polymers such as polyethylene in a relatively non-volatile solvent are extruded through an aperture (25) at constant concentration through the aperture and cooled to form a first gel of indefinite length (33). The first gels are extracted (D) with a volatile solvent to form a second gel (41) and the second gel is dried (E) to form a low porosity xerogel (47). The first gel, second gel or xerogel, or a combination, are stretched (F). Among the products obtainable are polyethylene fibers of greater than 38 or even 40 g/denier tenacity and of modulus greater than 1000 or even 1600 or 2000 g/denier.

FIG. 5
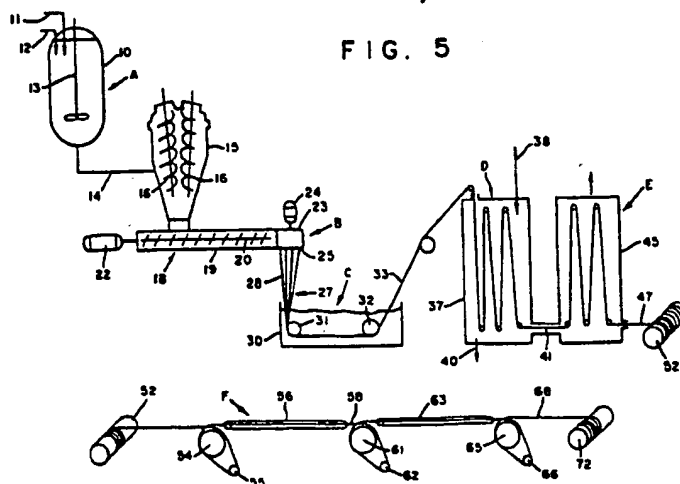
DESCRIPTION

PROCESS OF PRODUCING HIGH TENACITY, HIGH MODULUS CRYSTALLINE THERMOPLASTIC ARTICLE, AND NOVEL PRODUCT FIBERS

BACKGROUND OF THE INVENTION

The present invention relates to crystalline thermoplastic articles such as fibers or films having high tenacity, modulus and toughness values and a

5 process for their production which includes a gel intermediate.

The preparation of high strength, high modulus polyethylene fibers by growth from dilute solution has been described by U.S. Patent 4,137,394 to Meihuizen

10 et al. (1979) and pending U.S. application Serial No. 225,288 filed January 15, 1981.

Alternative methods to the preparation of high strength fibers have been described in various recent publications of P. Smith, A. J. Pennings and

15 their coworkers. German Off. 3004699 to Smith et al. (Aug. 21, 1980) describes a process in which polyethylene is first dissolved in a volatile solvent, the solution is spun and cooled to form a gel filament, and finally the gel filament is simultaneously stretched and

20 dried to form the desired fiber.

UK Patent application GB 2,051,667 to P. Smith and P. J. Lemstra (Jan. 21, 1981) discloses a process in which a solution of the polymer is spun and the filaments are drawn at a stretch ratio which is related to

25 the polymer molecular weight, at a drawing temperature

such that at the draw ratio used the modulus of the
filaments is at least 20 GPa. The application notes
that to obtain the high modulus values required, drawing
must be performed below the melting point of the poly-
ethylene. The drawing temperature is in general at most
135°C.

Kalb and Pennings in _Polymer_ _Bulletin_, vol. 1,
pp. 879-80 (1979), _Polymer_, 2584-90 (1980) and Smook et
al. in _Polymer Bull._, vol. 2, pp. 775-83 (1980) describe
a process in which the polyethylene is dissolved in a
nonvolatile solvent (paraffin oil) and the solution is
cooled to room temperature to form a gel. The gel is
cut into pieces, fed to an extruder and spun into a gel
filament. The gel filament is extracted with hexane to
remove the paraffin oil, vacuum dried and then stretched
to form the desired fiber.

In the process described by Smook et.al. and
Kalb and Pennings, the filaments were non-uniform, were
of high porosity and could not be stretched continuously
to prepare fibers of indefinite length.

BRIEF DESCRIPTION OF THE INVENTION

The present invention includes a process for
producing a shaped thermoplastic article of substan-
tially indefinite length (such as a fiber or film) which
comprises the steps:

a) forming a solution of a thermoplastic
crystalline polymer selected from the group consisting
of polyethylene, polypropylene, polyoxymethylene, poly-
butene-1, poly(vinylidine fluoride) and poly-4-methyl-
pentene-1 in a first, nonvolatile solvent at a first
concentration by weight of polymer per unit weight of
first solvent, said thermoplastic polymer having a
weight average molecular length between 7×10^4 and
80×10^4 backbone atoms and the solubility of said
thermoplastic polymer in said first solvent at a first
temperature being at least said first concentration;

b) extruding said solution through an aper-
ture, said solution being at a temperature no less than

said first temperature upstream of the aperture and being substantially at the first concentration both upstream and downstream of the aperture,

      c)   cooling the solution adjacent to and down-
stream of the aperture to a second temperature below the temperature at which a rubbery gel is formed, forming a gel containing first solvent of substantially indefinite length,

      d)   extracting the gel containing first sol-
vent with a second, volatile solvent for a sufficient contact time to form a gel containing second solvent which gel is substantially free of first solvent and is of substantially indefinite length;

      e)   drying the gel containing second solvent
to form a xerogel of substantially indefinite length free of first and second solvent; and

      f)   stretching at least one of:

         (i) the gel containing the first solvent,

         (ii) the gel containing the second solvent and,

         (iii) the xerogel,

at a total stretch ratio:

      (i) in the case of polyethylene which is
sufficient to achieve a tenacity of at least 20 g/denier and a modulus of at least 600 g/denier, and

      (ii) in the case of polypropylene which
is sufficient to achieve a tenacity of at least 10 g/denier and a modulus of at least 180 g/denier, and

      (iii) in the case of polyoxymethylene,
polybutene-1, poly(vinylidene fluoride) or poly (4-methylpentene-1) of at least 10:1.

The present invention also includes a poly-
ethylene fiber of substantially indefinite length being of weight average molecular weight at least 500,000 and having a tenacity of at least 20 g/denier, a tensile modulus at least 500 g/denier, a creep value no more than 5% (when measured at 10% of breaking load for 50 days at 23°C), a porosity less than 10% and a

melting temperature of at least 147°C.

The present invention also includes a poly-
ethylene fiber of substantially indefinite length being
of weight average molecular weight of at least 1,000,000
5   and having a tensile modulus of at least 1600 g/denier,
a melting point of at least 147°C and an elongation-to-
break of not more than 5%.

The present invention also includes a poly-
propylene fiber of substantially indefinite length
10 being of weight average molecular weight of at least
750,000 and having a tenacity of at least 8 g/denier, a
tensile modulus of at least 160 g/denier and a melting
temperature of at least 168°C.

The present invention also includes a poly-
15 olefin gel fiber of substantially indefinite length
comprising between 4 and 20 weight % solid polyethylene
of weight average molecular weight at least 500,000 or
solid polypropylene of weight average molecular weight
at least 750,000, and between 80 and 96 weight % of a
20 swelling solvent miscible with high boiling hydrocarbon
and having an atmospheric boiling point less than
50°C.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a graphic view of the tenacities
25 of polyethylene fibers prepared according to Examples
3-99 of the present invention versus calculated valves
therefore as indicated in the Examples. The numbers
indicate multiple points.

Figure 2 is a graphic view of the calculated
30 tenacities of polyethylene fibers prepared according to
the present invention as a function of polymer concen-
tration and draw ratio at a constant temperature of 140°C.

Figure 3 is a graphic view of the calculated
tenacities of polyethylene fibers prepared according to
35 the present invention as a function of draw temperature
and draw (or stretch) ratio at a constant polymer con-
centration of 4%.

Figure 4 is a graphic view of tenacity plotted

against tensile modulus for polyethylene fibers prepared in accordance with the present invention.

Figure 5 is a schematic view of a first process embodiment of the present invention.

Figure 6 is a schematic view of a second process embodiment of the present invention.

Figure 7 is a schematic view of a third process embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

There are many applications which require a load bearing element of high strength, modulus, toughness, dimensional and hydrolytic stability and high resistance to creep under sustained loads.

For example, marine ropes and cables, such as the mooring lines used to secure supertankers to loading stations and the cables used to secure deep sea drilling platforms to underwater anchorage, are presently constructed of materials such as nylon, polyester, aramids and steel which are subject to hydrolytic or corrosive attack by sea water. In consequence such mooring lines and cables are constructed with significant safety factors and are replaced frequently. The greatly increased weight and the need for frequent replacement create substantial operational and economic burdens.

The fibers and films of this invention are of high strength, extraordinarily high modulus and great toughness. They are dimensionally and hydrolytically stable and resistant to creep under sustained loads.

The fibers and films of the invention prepared according to the present process possess these properties in a heretofore unattained combination, and are therefore quite novel and useful materials.

Other applications for the fibers and films of this invention include reinforcements in thermoplastics, thermosetting resins, elastomers and concrete for uses such as pressure vessels, hoses, power transmission belts, sports and automotive equipment, and building construction.

In comparison to the prior art fibers prepared by Smith, Lemstra and Pennings described in Off 30 04 699, GB 205,1667 and other cited references, the strongest fibers of the present invention are of higher melting point, higher tenacity and much higher modulus. Additionally, thay are more uniform, and less porous than the prior art fibers.

In comparison with Off 30 04 699 to Smith et.al. the process of the present invention has the advantage of greater controllability and reliability in that the steps of drying and stretching may be separate and each step may be carried out under optimal conditions. To illustrate, Smith & Lemstra in _Polymer Bulletin_, vol. 1, pp. 733-361 (1979) indicate that drawing temperature, below 143°C, had no effect on the relationships between either tenacity or modulus and stretch ratio. As will be seen, the properties of the fibers of the present invention may be controlled in part by varying stretch temperature with other factors held constant.

In comparison with the procedures described by Smook et.al in _Polymer Bulletin_, vol. 2, pp. 775-83 (1980) and in the above Kalb and Pennings articles, the process of the present invention has the advantage that the intermediate gel fibers which are spun are of uniform concentration and this concentration is the same as the polymer solution as prepared. The advantages of this unformity are illustrated by the fact that the fibers of the present invention may be stretched in a continuous operation to prepare packages of indefinite length. Additionally, the intermediate xerogel fibers of the present invention preferably contain less than 10 volume % porosity compared to 23-65% porosity in the dry gel fibers described by _Smook et al._ and _Kalb and Pennings_.

The crystallizable polymer used in the present invention may be a polyolefin such as polyethylene, polypropylene or poly(methylpentene-1) or may be another

polymer such as poly(oxymethylene) or poly(vinylidene fluoride). In the case of polyethylene, suitable polymers have molecular weights (by intrinsic viscosity) in the range of one to ten million. This corres-
ponds to a weight average chain length of 3.6×10^4 to 3.6×10^5 monomer units or 7×10^4 to 7.1×10^5 carbons. Other polyolefins and poly(haloolefins) should have similar backbone carbon chain lengths. For polymers such as poly(oxymethylene) the total chain length should preferably be in the same general range, i.e. 7×10^4 to 71×10^4 atoms, with some adjustment possible due to the differences in bond angles between C-C-C and C-O-C.

The weight average molecular weight of polyethylene used is at least 500,000 (6 IV), preferably at least 1,000,000 (10 IV), and more preferably between 2,000,000 (16 IV) and 8,000,000 (42 IV). The weight average molecular weight of polypropylene used is at least 750,000 (5 IV), preferably at least 1,000,000 (6 IV), more preferably at least 1,500,000 (9 IV) and most preferably between 2,000,000 (11 IV) and 8,000,000 (33 IV). The IV numbers represent intrinsic viscosity of the polymer in decalin at 135°C.

The first solvent should be non-volatile under the processing conditions. This is necessary in order to maintain essentially constant the concentration of solvent upstream and through the aperture (die) and to prevent non-uniformity in liquid content of the gel fiber or film containing first solvent. Preferably, the vapor pressure of the first solvent should be no more than 20 kPa (one-fifth of an atmosphere) at 175°C, or at the first temperature. Preferred first solvents for hydrocarbon polymers are aliphatic and aromatic hydrocarbons of the desired non-volatility and solubility for the polymer. The polymer may be present in the first solvent at a first concentration which is selected from a relatively narrow range, e.g. 2 to 15 weight percent, preferably 4 to 10 weight percent and more preferably 5 to 8 weight percent; however, once chosen, the concen-

tration should not vary adjacent the die or otherwise
prior to cooling to the second temperature. The con-
centration should also remain reasonably constant over
time (i.e. length of the fiber or film).

5   The first temperature is chosen to achieve
complete dissolution of the polymer in the first
solvent. The first temperature is the minimum tempera-
ture at any point between where the solution is formed
and the die face, and must be greater than the gelation

10   temperature for the polymer in the solvent at the first
concentration. For polyethylene in paraffin oil at 5-15%
concentration, the gelation temperature is approxi-
mately 100-130°C; therefore, a preferred first tempera-
ture can be between 180°C and 250°C, more preferably

15   200-240. While temperatures may vary above the first
temperature at various points upstream of the die face,
excessive temperatures causitive of polymer degradation
should be avoided. To assure complete solubility, a
first temperature is chosen whereat the solubility of

20   the polymer exceeds the first concentration, and is
typically at least 100% greater. The second temperature
is chosen whereas the solubility of the polymer is much
less than the first concentration. Preferably, the
solubility of the polymer in the first solvent at the

25   second temperature is no more than 1% of the first con-
centration. Cooling of the extruded polymer solution
from the first temperature to the second temperature
should be accomplished at a rate sufficiently rapid to
form a gel fiber which is of substantially the same

30   polymer concentration as existed in the polymer solu-
tion. Preferably the rate at which the extruded polymer
solution is cooled from the first temperature to the
second temperature should be at least 50°C per minute.
          Some stretching during cooling to the second

35   temperature is not excluded from the present invention,
but the total stretching during this stage should not
normally exceed 2:1, and preferably no more than
1.5:1. As a result of those factors the gel fiber

formed upon cooling to the second temperature consists
of a continuous polymeric network highly swollen with
solvent. The gel usually has regions of high and low
polymer density on a microscopic level but is generally
5 free of large (greater than 500 nm) regions void of
solid polymer.

If an aperture of circular cross section (or
other cross section without a major axis in the plane
perpendicular to the flow direction more than 8 times
10 the smallest axis in the same plane, such as oval, Y- or
X-shaped aperature) is used, then both gels will be gel
fibers, the xerogel will be an xerogel fiber and the
thermoplastic article will be a fiber. The diameter
of the aperture is not critical, with representative
15 aperatures being between 0.25 mm and 5 mm in
diameter (or other major axis). The length of the aper-
ture in the flow direction should normally be at least
10 times the diameter of the aperture (or other
similar major axis), perferably at least 15 times and
20 more preferably at least 20 times the diameter (or other
similar major axis).

If an aperture of rectangular cross section is
used, then both gels will be gel films, the xerogel will
be a xerogel film and the thermoplastic article will be
25 a film. The width and height of the aperture are not
critical, with representative apertures being between
2.5 mm and 2 m in width (corresponding to film width),
between 0.25 mm and 5 mm in height (corresponding to
film thickness). The depth of the aperture (in the flow
30 direction) should normally be at least 10 times the
height of the aperture, preferably at least 15 times the
height and more preferably at least 20 times the height.

The extraction with second solvent is con-
ducted in a manner that replaces the first solvent in
35 the gel with second solvent without significant changes
in gel structure. Some swelling or shrinkage of the gel
may occur, but preferably no substantial dissolution,
coagulation or precipitation of the polymer occurs.

-10-

When the first solvent is a hydrocarbon, suitable second solvents include hydrocarbons, chlorinated hydrocarbons, chlorofluorinated hydrocarbons and others, such as pentane, hexane, heptane, toluene, methylene

5 chloride, carbon tetrachloride, trichlorotrifluoroethane (TCTFE), diethyl ether and dioxane.

The most preferred second solvents are methylene chloride (B.P. 39.8°C) and TCFE (B.P. 47.5°C). Preferred second solvents are the non-flammable volatile

10 solvents having an atmospheric boiling point below 80°C, more preferably below 70°C and most preferably below 50°C. Conditions of extraction should remove the first solvent to less than 1% of the total solvent in the gel.

A preferred combination of conditions is a

15 first temperature between 150°C and 250°C, a second temperature between -40°C and 40°C and a cooling rate between the first temperature and the second temperature of at least 50°C/minute. It is preferred that the first solvent be a hydrocarbon, when the polymer is a

20 polyolefin such as ultrahigh molecular weight polyethylene. The first solvent should be substantially non-volatile, one measure of which is that its vapor pressure at the first temperature should be less than one-fifth atmosphere (20 kPa), and more preferably less

25 than 2 kPa.

In choosing the first and second solvents, the primary desired difference relates to volatility as discussed above. It is also preferred that the polymers be less soluble in the second solvent at 40°C than in

30 the first solvent at 150°C.

Once the gel containing second solvent is formed, it is then dried under conditions where the second solvent is removed leaving the solid network of polymer substantially intact. By analogy to silica

35 gels, the resultant material is called herein a "xerogel" meaning a solid matrix corresponding to the solid matrix of a wet gel, with the liquid replaced by gas (e.g. by an inert gas such as nitrogen or by air).

The term "xerogel" is not intended to delineate any
particular type of surface area, porosity or pore size.

A comparison of the xerogels of the present
invention with corresponding dried gel fibers prepared
5   according to prior art indicates the following major
differences in structure: The dried xerogel fibers of
the present invention preferably contain less than ten
volume percent pores compared to approximately 55 volume
percent pores in the Kalb and Pennings dried gel fibers
10   and approximately 23-65 volume percent pores in the
Smook et al. dried gel fibers. The dried xerogel fibers
of the present invention show a surface area (by the
B.E.T. technique) of less than 1 m^2/g as compared to
28.8 m^2/g in a fiber prepared by the prior art method
15   (see Comparative Example 1 and Example 2, below).

The xerogel fibers of the present invention
are also novel compared to dry, unstretched fibers of
GB 2,051,667 and Off. 3004699 and related articles by
Smith and Lemstra. This difference is evidenced by the
20   deleterious effect of stretching below 75°C or above
135°C upon the Smith and Lemstra unstretched fibers. In
comparison, stretching of the present xerogel fibers at
room temperature and above 135°C has beneficial rather
than deleterious effects (see, for example, Examples
25   540-542, below). While the physical nature of these
differences are not clear because of lack of information
about Smith and Lemstra's unstretched fibers, it appears
that one or more of the following characteristics of the
present xerogel fibers must be lacking in Smith and
30   Lemstra's unstretched fibers: (1) a crystalline
orientation function less than 0.2, and preferably less
than 0.1 as measured by wide angle X-ray diffraction;
(2) microporosity less than 10% and preferrably less
than 3%; (3) a crystallinity index as measured by wide

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angle X-ray diffraction (see P. H. Hermans and A. Weidinger, _Macromol. Chem._ vol. 44, p. 24 (1961)) less than 80% and preferably less than 75%; (4) no detectable fraction of the triclinic crystalline form and (5) a

5   fraction variation of the spherulite size across a diameter of the fiber less than 0.25.

Stretching may be performed upon the gel fiber after cooling to the second temperature or during or after extraction. Alternatively, stretching of the

10   xerogel fiber may be conducted, or a combination of gel stretch and xerogel stretch may be performed. The stretching may be conducted in a single stage or it may be conducted in two or more stages. The first stage stretching may be conducted at room temperatures or at

15   an elevated temperature. Preferably the stretching is conducted in two or more stages with the last of the stages performed at a temperature between 120°C and 160°C. Most preferably the stretching is conducted in at least two stages with the last of the stages per-

20   formed at a temperature between 135°C and 150°C. The Examples, and especially Examples 3-99 and 111-486, illustrate how the stretch ratios can be related to obtaining particular fiber properties.

The product polyethylene fibers produced by

25   the present process represent novel articles in that they include fibers with a unique combination of properties: a modulus at least 500 g/denier (preferably at least 1000 g/denier, more preferably at least 1600 g/denier and most preferably at least 2000 g/denier),

30   a tenacity at least 20 g/denier (preferably at least 30 g/denier and more preferably at least 40 g/denier), a melting temperature of at least 147°C (preferably at least 149°C), a porosity of no more than 10% (preferably no more than 6%) and a creep value no more than 5%

35   (preferably no more than 3%) when measured at 10% of breaking load for 50 days at 23°C. Preferably the fiber has an elongation to break at most 7%. In addition, the fibers have high toughness and uniformity. These

additional properties can be measured as a workto-break
value preferably at least 7.5 gigajoules per cubic
meter. Furthermore, as indicated in Examples 3-99 and
111-489 below, trade-offs between various properties can
be made in a controlled fashion with the present

5   process.

The novel polypropylene fibers of the present
invention also include a unique combination of proper-
ties, previously unachieved for polypropylene fibers: a
tenacity of at least 8 g/denier (preferably at least

10 11 g/denier and more preferably at least 13 g/denier),
a tensile modulus at least 160 g/denier (preferably at
least 200 g/denier), a main melting point at least 168°C
(preferably at least 170°C) and a porosity less than
10% (preferably no more than 5%). Preferably, the

15 polypropylene fibers also have an elongation to break
less than 20%.

Additionally a novel class of fibers of the inven-
tion are polypropylene fibers possessing a modulus of at
least 200 g/denier, preferably at least 220 g/denier.

20 The gel fibers containing first solvent, gel
fibers containing second solvent and xerogel fibers of
the present invention also represent novel articles of
manufacture, distinguished from somewhat similar pro-
ducts described by Smook et al. and by Kalb and Pennings

25 in having a volume porosities of 10% or less compared to
values of 23%-65% in the references.

In particular the second gel fibers differ
from the comparable prior art materials in having a
solvent with an atmospheric boiling point less than

30 50°C. As indicated by Examples 100-108, below, the
uniformity and cylindrical shape of the xerogel fibers
improved progressively as the boiling point of the
second solvent declined. As also indicated in Examples
100-108 (see Table III), substantially higher tenacity

35 fibers were produced under equivalent drying and
stretching conditions by using trichlorotrifluoroethane
(boiling point 47.5°C) as the second solvent compared to
fibers produced by using hexane (boiling point 68.7°C)

as second solvent. The improvement in final fiber is then directly attributable to changes in the second solvent in the second gel fiber. Preferred such second solvents are halogenated hydrocarbons of the proper boiling point such as methylene chloride (dichloromethane) and trichlorotrifluoroethane, with the latter being most preferred.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Figure 5 illustrates in schematic form a first embodiment of the present invention, wherein the stretching step F is conducted in two stages on the xerogel fiber subsequent to drying step E. In Figure 5, a first mixing vessel 10 is shown, which is fed with an ultra high molecular weight polymer 11 such as polyethylene of weight average molecular weight at least 500,000 and preferably at least 1,000,000, and to which is also fed a first, relatively non-volatile solvent 12 such as paraffin oil. First mixing vessel 10 is equipped with an agitator 13. The residence time of polymer and first solvent in first mixing vessel 10 is sufficient to form a slurry containing some dissolved polymer and some relatively finely divided polymer particles, which slurry is removed in line 14 to an intensive mixing vessel 15. Intensive mixing vessel 15 is equipped with helical agitator blades 16. The residence time and agitator speed in intensive mixing vessel 15 is sufficient to convert the slurry into a solution. It will be appreciated that the temperature in intensive mixing vessel 15, either because of external heating, heating of the slurry 14, heat generated by the intensive mixing, or a combination of the above is sufficiently high (e.g. 200°C) to permit the polymer to be completely dissolved in the solvent at the desired concentration (generally between 6 and 10 percent polymer, by weight of solution). From the intensive mixing vessel 15, the solution is fed to an extrusion device 18, containing a barrel 19 within which is a screw 20 operated by motor 22 to deliver polymer solution at reasonably high pres-

sure to a gear pump and housing 23 at a controlled flow
rate. A motor 24 is provided to drive gear pump 23 and
extrude the polymer solution, still hot, through a spin-
nerette 25 comprising a plurality of aperatures, which
may be circular, X-shaped, or, oval-shaped, or in any of
5   a variety of shapes having a relatively small major axis
in the plane of the spinnerette when it is desired to
form fibers, and having a rectangular or other shape
with an extended major axis in the plane of the spinner-
ette when it is desired to form films. The temperature
10   of the solution in the mixing vessel 15, in the extru-
sion device 18 and at the spinnerette 25 should all
equal or exceed a first temperature (e.g. 200°C) chosen
to exceed the gellation temperature (approximately
100-130°C for polyethylene in paraffin oil). The temp-
15   erature may vary (e.g. 220°C, 210°C and 200°C) or may be
constant (e.g. 220°C) from the mixing vessel 15 to extr-
usion device 18 to the spinnerette 25. At all points,
however, the concentration of polymer in the
solution should be substantially the same. The
20   number of aperatures, and thus the number of fibers
formed, is not critical, with convenient numbers of
apperatures being 16, 120, or 240.
          From the spinnerette 25, the polymer solution
passes through an air gap 27, optionally enclosed and
25   filled with an inert gas such as nitrogen, and option-
ally provided with a flow of gas to facilitate cooling.
A plurality of gel fibers 28 containing first solvent
pass through the air gap 27 and into a quench bath 30,
so as to cool the fibers, both in the air gap 27 and in
30   the quench bath 30, to a second temperature at which the
solubility of the polymer in the first solvent is rela-
tively low, such that most of the polymer precipitates
as a gel material. While some stretching in the air gap
27 is permissible, it is preferably less than 2:1, and
35   is more preferably much lower. Substantial stretching
of the hot gel fibers in air gap 27 is believed highly
detrimental to the properties of the ultimate fibers.
          It is preferred that the quench liquid in

quench bath 30 be water. While the second solvent may
be used as the quench fluid (and quench bath 30 may even
be integral with solvent extraction device 37 described
below), it has been found in limited testing that such a
5   modification impairs fiber properties.

Rollers 31 and 32 in the quench bath 30 oper-
rate to feed the fiber through the quench bath, and
preferably operate with little or no stretch. In the
event that some stretching does occur across rollers 31
10 and 32, some first solvent exudes out of the fibers and
can be collected as a top layer in quench bath 30.

From the quench bath 30, the cool first gel
fibers 33 pass to a solvent extraction device 37 where a
second solvent, being of relatively low boiling such as
15 trichlorotrifluoroethane, is fed in through line 38.
The solvent outflow in line 40 contains second solvent
and essentially all of the first solvent brought in with
the cool gel fibers 33, either dissolved or dispersed in
the second solvent. Thus the second gel fibers 41
20 conducted out of the solvent extraction device 37
contain substantially only second solvent, and
relatively little first solvent. The second gel fibers
41 may have shrunken somewhat compared to the first gel
fibers 33, but otherwise contain substantially the same
25 polymer morphology.

In a drying device 45, the second solvent is
evaporated from the second gel fibers 41 forming
essentially unstretched xerogel fibers 47 which are
taken up on spool 52.

30 From spool 52, or from a plurality of such
spools if it is desired to operate the stretching line
at a slower feed rate than the take up of spool 52
permits, the fibers are fed over driven feed roll 54 and
idler roll 55 into a first heated tube 56, which may be
35 rectangular, cylindrical or other convenient shape.
Sufficient heat is applied to the tube 56 to cause the
internal temperature to be between 120 and 140°C.
The fibers are stretched at a relatively high draw ratio

(e.g. 10:1) so as to form partially stretched fibers 58
taken up by driven roll 61 and idler roll 62. From
rolls 61 and 62, the fibers are taken through a second
heated tube 63, heated so as to be at somewhat higher

5   temperature, e.g. 130-160°C and are then taken up by
driven take-up roll 65 and idler roll 66, operating at a
speed suficient to impart a stretch ratio in heated tube
63 as desired, e.g. 2.5:1. The twice stretched
fibers 68 produced in this first embodiment are taken up

10   on take-up spool 72.

             With reference to the six process steps of the
present invention, it can be seen that the solution
forming step A is conducted in mixers 13 and 15. The
extruding step B is conducted with device 18 and 23, and

15   especially through spinnerette 25. The cooling step C
is conducted in airgap 27 and quench bath 30. Extrac-
tion step D is conducted in solvent extraction device
37. The drying step E is conducted in drying device
45. The stretching step F is conducted in elements 52-

20   72, and especially in heated tubes 56 and 63. It will
be appreciated, however, that various other parts of the
system may also perform some stretching, even at
temperatures substantially below thase of heated tubes
56 and 63. Thus, for example, some stretching (e.g.

25   2:1) may occur within quench bath 30, within solvent
extraction device 37, within drying device 45 or between
solvent extraction device 37 and drying device 45.

             A second embodiment of the present invention
is illustrated in schematic form by Figure 6. The

30   solution forming and extruding steps A and B of the
second embodiment are substantially the same as those in
the first embodiment illustrated in Figure 5. Thus,
polymer and first solvent are mixed in first mixing
vessel 10 and conducted as a slurry in line 14 to

35   intensive mixing device 15 operative to form a hot
solution of polymer in first solvent. Extrusion device
18 impells the solution under pressure through the gear
pump and housing 23 and then through a plurality of

apperatures in spinnerette 27. The hot first gel fibers 28 pass through air gap 27 and quench bath 30 so as to form cool first gel fibers 33.

The cool first gel fibers 33 are conducted
5   over driven roll 54 and idler roll 55 through a heated tube 57 which, in general, is longer than the first heated tube 56 illustrated in Figure 5. The length of heated tube 57 compensates, in general, for the higher velocity of fibers 33 in the second embodiment of
10 Figure 6 compared to the velocity of xerogel fibers (47) between take-up spool 52 and heated tube 56 in the first embodiment of Figure 5. The fibers 33 are drawn through heated tube 57 by driven take-up roll 59 and idler roll 60, so as to cause a relatively high stretch
15 ratio (e.g. 10:1). The once-stretched first gel fibers 35 are conducted into extraction device 37.

In the extraction device 37, the first solvent is extracted out of the gel fibers by second solvent and the gel fibers 42 containing second solvent are con-
20 ducted to a drying device 45. There the second solvent is evaporated from the gel fibers; and xerogel fibers 48, being once-stretched, are taken up on spool 52.

Fibers on spool 52 are then taken up by driven feed roll 61 and idler 62 and passed through a heated
25 tube 63, operating at the relatively high temperature of between 130 and 160°C. The fibers are taken up by driven take up roll 65 and idler roll 66 operating at a speed sufficient to impart a stretch in heated tube 63 as desired, e.g. 2.5:1. The twice-stretched fibers
30 69 produced in the second embodiment are then taken up on spool 72.

It will be appreciated that, by comparing the embodiment of Figure 6 with the embodiment of Figure 5, the stretching step F has been divided into two parts,
35 with the first part conducted in heated tube 57 per- formed on the first gel fibers 33 prior to extraction (D) and drying (E), and the second part conducted in heated tube 63, being conducted on xerogel fibers 48

subsequent to drying (E).

The third embodiment of the present invention is illustrated in Figure 7, with the solution forming step A, extrusion step B, and cooling step C being sub-
5 stantially identical to the first embodiment of Figure 5 and the second embodiment of Figure 6. Thus, polymer and first solvent are mixed in first mixing vessel 10 and conducted as a slurry in line 14 to intensive mixing device 15 operative to form a hot solution of polymer in
10 first solvent. Extrusion device 18 impells the solution under pressure through the gear pump and housing 23 and then through a plurality of apperatures in spinnerette 27. The hot first gel fibers 28 pass through air gap 27 and quench bath 30 so as to form cool first gel fibers
15 33.

The cool first gel fibers 33 are conducted over driven roll 54 and idler roll 55 through a heated tube 57 which, in general, is longer than the first heated tube 56 illustrated in Figure 5. The length of
20 heated tube 57 compensates, in general, for the higher velocity of fibers 33 in the third embodiment of Figure 7 compared to the velocity of xerogel fibers (47) between takeup spool 52 and heated tube 56 in the first embodiment of Figure 5. The first gel fibers 33 are now
25 taken up by driven roll 61 and idler roll 62, operative to cause the stretch ratio in heated tube 57 to be as desired, e.g. 10:1.

From rolls 61 and 62, the once-drawn first gel fibers 35 are conducted into modified heated tube 64 and
30 drawn by driven take up roll 65 and idler roll 66. Driven roll 65 is operated sufficiently fast to draw the fibers in heated tube 64 at the desired stretch ratio, e.g. 2.5:1. Because of the relatively high line speed in heated tube 64, required generally to match the speed
35 of once-drawn gel fibers 35 coming off of rolls 61 and 62, heated tube 64 in the third embodiment of figure 7 will, in general, be longer than heated tube 63 in either the second embodiment of Figure 6 or the first

embodiment of Figure 5. While first solvent may exude from the fiber during stretching in heated tubes 57 and 64 (and be collected at the exit of each tube), the first solvent is sufficiently non-volatile so as not to
5 evaporate to an appreciable extent in either of these heated tubes.

The twice-stretched first gel fiber 36 is then conducted through solvent extraction device 37, where the second, volatile solvent extracts the first solvent
10 out of the fibers. The second gel fibers, containing substantially only second solvent, is then dried in drying device 45, and the twice-stretched fibers 70 are then taken up on spool 72.

It will be appreciated that, by comparing the
15 third embodiment of Figure 7 to the first two embodiments of Figures 5 and 6, the stretching step (F) is performed in the third embodiment in two stages, both subsequent to cooling step C and prior to solvent extracting step D.

20 The process of the invention will be further illustrated by the examples below. The first example illustrates the prior art techniques of Smook et.al. and the Kalb and Pennings articles.

Comparative Example 1

25 A glass vessel equipped with a PTFE paddle stirrer was charged with 5.0 wt% linear polyethylene (sold as Hercules UHMW 1900, having 24 IV and approximately 4×10^6 M.W.), 94.5 wt% paraffin oil (J.T. Baker, 345-355 Saybolt viscosity) and 0.5 wt% antioxi-
30 dant (sold under the trademark Ionol).

The vessel was sealed under nitrogen pressure and heated with stirring to 150°C. The vessel and its contents were maintained under slow agitation for 48 hours. At the end of this period the solution was
35 cooled to room temperature. The cooled solution separated into two phases - A "mushy" liquid phase consisting of 0.43 wt% polyethylene and a rubbery gel phase consisting of 8.7 wt% polyethylene. The gel phase was

collected, cut into pieces and fed into a 2.5 cm (one
inch) Sterling extruder equipped with a 21/1 L/D
polyethylene-type screw. The extruder was operated at
10 RPM, 170°C and was equipped with a conical single
5   hole spinning die of 1 cm inlet diameter, 1 mm exit
diameter and 6 cm length.

    The deformation and compression of the gel by
the extruder screw caused exudation of paraffin oil from
the gel. This liquid backed up in the extruder barrel
10   and was mostly discharged from the hopper end of the
extruder. At the exit end of the extruder a gel fiber
of approximately 0.7 mm diameter was collected at the
rate of 1.6 m/min. The gel fiber consisted of 24-38 wt%
polyethylene. The solids content of the gel fiber
15   varied substantially with time.

    The paraffin oil was extracted from the
extruded gel fiber using hexane and the fiber was dried
under vacuum at 50°C. The dried gel fiber had a density
of 0.326 g/cm^3. Therefore, based on a density of 0.960
20   for the polyethylene constituent, the gel fiber con-
sisted of 73.2 volume percent voids. Measurement of
pore volume using a mercury porosimeter showed a pore
volume of 2.58 cm^3/g. A B.E.T. measurement of surface
area gave a value of 28.8 m^2/g.
25   The dried fiber was stretched in a nitrogen
atmosphere within a hot tube of 1.5 meters length.
Fiber feed speed was 2 cm/min. Tube temperature was
100°C at the inlet increasing to 150°C at the outlet.

    It was found that, because of filament non-
30   uniformity, stretch ratios exceeding 30/1 were not sus-
tainable for periods exceeding 20 minutes without
filament breakage.

    The properties of the fiber prepared at 30/1
stretch ratio were as follows:
35   denier - 99

              tenacity - 23 g/d

              modulus - 980 g/d

              elongation at break - 3%

-22-

work-to-break - 6570 in lbs./in^3

(6.5 x 10^9 J/m^3 or 6.5 GJ/m^3)

The following example is illustrative of the present invention:

5   Example 2

An oil jacketed double helical (Helicone®) mixer constructed by Atlantic Research Corporation was charged with 5.0 wt% linear polyethylene (Hercules UHMW 1900 having a 17 IV and approximately 2.5 x 10^6 M.W.)

10   and 94.5 wt% paraffin oil (J.T. Baker, 345-355 Saybolt viscosity). The charge was heated with agitation at 20 rpm to 200°C under nitrogen pressure over a period of two hours. After reaching 200°C, agitation was maintained for an additional two hours.

15   The bottom discharge opening of the Helicone mixer was fitted with a single hole capillary spinning die of 2 mm diameter and 9.5 mm length. The temperature of the spinning die was maintained at 200°C.

Nitrogen pressure applied to the mixer and

20   rotation of the blades of the mixer were used to extrude the charge through the spinning die. The extruded uniform solution filament was quenched to a gel state by passage through a water bath located at a distance of 33 cm (13 inches) below the spinning die. The gel filament

25   was wound up continuously on a 15.2 cm (6 inch) diameter bobbin at the rate of 4.5 meters/min.

The bobbins of gel fiber were immersed in trichlorotrifloroethane (fluorocarbon 113 or "TCTFE") to exchange this solvent for paraffin oil as the liquid

30   constituent of the gel. The gel fiber was unwound from a bobbin, and the fluorocarbon solvent evaporated at 22-50°C.

The dried fiber was of 970 ± 100 denier. The density of the fiber was determined to be 950 kg/m^3 by

35   the density gradient method. Therefore, based on a density of 960 kg/m^3 for the polyethylene constituent, the dried fiber contained one volume percent voids. A B.E.T. measurement of the surface area gave a value less

than 1 m^2/g.

The dried gel fiber was fed at 2 cm/min into a hot tube blanketed with nitrogen and maintained at 100°C at its inlet and 140°C at its outlet. The fiber was stretched continously 45/1 within the hot tube for a period of three hours without experiencing fiber breakage. The properties of the stretched fiber were:

denier - 22.5
tenacity - 37.6 g/d
modulus - 1460 g/d
elongation - 4.1%
work-to-break - 12,900 in-lbs/in
(12.9 x 10^9 J/m^3 or 12.9 GJ/m^3)

Examples 3-99

A series of fiber samples was prepared following the procedures described in Example 2, but with variations introduced in the following material and process parameters:

a. polyethylene IV (molecular weight)
b. polymer gel concentration
c. stretch temperature
d. fiber denier
e. stretch ratio

The results of these experiments upon the final fiber properties obtained are presented in Table I. The Polymer intrinsic viscosity values were 24 in Examples 3-49 and 17 in Examples 50-99. The gel concentration was 2% in Examples 26-41, 4% in Examples 3-17, 5% in Examples 42-99 and 6% in Examples 18-25.

TABLE I

Ex.	Stretch Temp., °C	Stretch Ratio	Denier	Tenacity g/d	Modulus g/d	Elong %	Work-to-Break GJ/m³
3	142	15.6	2.8	17.8	455.	6.7	9.4
4	145	15.5	2.8	18.6	480.	6.7	10.1
5	145	19.6	2.2	19.8	610.	5.2	8.1
6	145	13.0	3.4	13.7	350.	6.2	7.0
7	145	16.6	2.7	15.2	430.	5.7	6.6
8	144	23.9	1.8	23.2	730.	4.9	9.2
9	150	16.0	2.7	14.6	420.	5.0	5.8
10	150	27.3	1.6	21.6	840.	4.0	7.0
11	149	23.8	1.8	21.8	680.	4.6	8.0
12	150	27.8	1.6	22.6	730.	4.3	7.5
13	140	14.2	3.1	16.5	440.	5.3	7.1
14	140	22.0	2.0	21.7	640.	4.7	8.5
15	140	25.7	1.7	26.1	810.	4.7	10.2
16	140	3.4	5.6	11.2	224.	18.0	10.7
17	140	14.9	2.9	20.8	600.	5.6	10.0
18	145	19.5	11.7	16.4	480.	6.3	8.2
19	145	11.7	19.4	16.3	430.	6.1	7.7
20	145	22.3	10.2	24.1	660.	5.7	11.2
21	145	47.4	4.8	35.2	1230.	4.3	12.2
22	150	15.1	15.0	14.0	397.	6.5	6.5
23	150	56.4	4.0	28.2	830.	4.4	10.6
24	150	52.8	4.3	36.3	1090	4.5	15.2
25	150	12.8	17.8	19.1	440.	7.2	11.3
26	143	10.3	21.4	8.7	178.	7.0	4.8
27	146	1.8	120.0	2.1	22.	59.7	12.5
28	146	3.2	69.5	2.7	37.	40.5	11.2
29	145	28.0	7.9	16.0	542.	4.9	6.4
30	145	50.2	4.4	21.6	725.	4.0	7.4
31	145	30.7	7.2	22.7	812.	4.2	7.8
32	145	10.2	21.8	16.2	577.	5.6	8.7
33	145	22.3	9.9	15.3	763.	2.8	4.0
34	150	28.7	7.7	10.5	230.	8.4	7.4
35	150	12.1	18.3	12.6	332.	5.2	5.5
36	150	8.7	25.5	10.9	308.	5.9	5.5

TABLE I (continued)

	Ex.	Stretch Temp., °C	Stretch Ratio	Denier	Tenacity g/d	Modulus g/d	Elong %	Work-to-Break GJ/m³
5	37	150	17.4	12.7	14.1	471.	4.6	5.3
	38	140	12.0	18.5	12.7	357.	7.3	8.1
	39	140	21.5	10.3	16.1	619.	4.2	5.5
	40	140	36.8	6.0	23.8	875.	4.1	7.8
	41	140	59.7	3.7	26.2	1031.	3.6	7.0
10	42	145	13.4	25.0	12.9	344.	8.3	9.2
	43	145	24.4	13.7	22.3	669.	5.9	11.4
	44	145	25.2	13.3	23.2	792.	4.9	9.8
	45	145	33.5	10.0	29.5	1005.	4.9	11.8
	46	150	17.2	19.5	14.2	396.	5.6	6.8
15	47	150	16.0	21.0	15.7	417.	7.2	9.5
	48	140	11.2	30.0	13.1	316.	8.3	9.6
	49	140	21.0	16.0	23.0	608.	6.0	12.4
	50	130	15.8	64.9	14.2	366.	6.0	6.8
	51	130	44.5	23.1	30.8	1122.	4.4	10.8
20	52	130	24.3	42.4	26.8	880.	4.7	10.5
	53	130	26.5	38.8	23.6	811.	4.2	7.9
	54	140	11.0	93.3	14.5	303.	8.4	9.8
	55	140	28.3	36.3	24.7	695.	4.8	9.4
	56	140	43.4	23.7	30.3	905.	4.8	11.7
25	57	140	18.4	55.9	19.7	422.	6.6	10.3
	58	150	15.7	65.5	12.8	337.	8.6	9.9
	59	150	43.4	23.7	30.9	1210.	4.5	12.4
	60	150	33.6	30.6	28.9	913.	4.8	11.7
	61	150	54.4	18.9	30.2	1134.	3.7	10.9
30	62	150	13.6	71.1	10.4	272.	12.2	12.0
	63	150	62.9	15.4	30.5	1008.	4.0	11.5
	64	150	26.6	36.4	20.4	638.	7.0	13.0
	65	150	36.1	26.8	32.0	1081.	5.3	13.4
	66	150	52.0	18.6	34.0	1172.	4.1	12.6
35	67	150	73.3	13.2	35.3	1314.	3.8	12.3
	68	140	14.6	66.1	13.9	257.	14.9	18.1
	69	140	30.1	32.1	28.5	933.	4.5	11.4
	70	140	45.6	21.2	35.9	1440.	3.9	8.8

TABLE I (continued)

Ex.	Stretch Temp., °C	Stretch Ratio	Denier	Tenacity g/d	Modulus g/d	Elong %	Work-to-Break GJ/m³
71	140	43.0	22.5	37.6	1460.	4.1	12.8
72	140	32.2	30.1	33.1	1170.	4.3	12.0
73	140	57.3	16.9	39.6	1547.	3.8	13.4
74	130	16.3	59.4	21.6	556.	5.5	10.6
75	130	20.6	47.0	25.6	752.	5.3	12.0
76	130	36.3	26.7	33.0	1144.	4.1	12.4
77	130	49.4	19.6	30.4	1284.	3.8	11.6
78	130	24.5	44.6	26.4	990.	4.5	9.7
79	130	28.6	38.2	27.1	975.	4.5	10.5
80	130	42.2	25.9	34.7	1200.	4.4	12.5
81	140	40.3	27.1	33.2	1260.	4.0	11.4
82	140	58.7	18.6	35.5	1400.	4.0	10.8
83	145	47.9	22.8	32.1	1460.	4.0	10.0
84	145	52.3	20.9	37.0	1500.	4.0	12.2
85	130	13.6	80.4	12.8	275.	8.0	8.7
86	130	30.0	36.4	24.8	768.	5.0	10.6
87	130	29.7	36.8	28.6	1005.	4.5	11.5
88	140	52.0	21.0	36.0	1436.	3.5	12.1
89	140	11.8	92.3	10.1	151.	18.5	18.3
90	140	35.3	31.0	29.8	1004.	4.5	10.3
91	140	23.4	46.8	26.6	730.	5.5	12.6
92	150	14.6	74.9	11.5	236.	11.0	11.2
93	150	35.7	30.6	27.4	876.	4.5	10.0
94	150	31.4	34.8	27.0	815.	5.0	10.7
95	150	37.8	28.9	29.8	950.	4.5	10.7
96	150	15.9	68.7	9.8	210.	10.0	8.2
97	150	30.2	36.2	24.6	799.	5.0	9.4
98	150	36.1	30.3	28.2	959.	4.5	10.0
99	150	64.7	16.9	32.1	1453.	3.5	8.6

In order to determine the relationships of
the fiber properties to the process and material para-
meters, the data of Table I were subjected to statis-
tical analysis by multiple lnear regression. The
5   regression equation obtained for fiber tenacity was as
follows:

Tenacity, g/d = -8.47 + 2.00 * SR + 0.491 * IV + 0.0605 * C * SR
                0.00623 *T*SR- 0.0156*IV*SR - 0.00919 * SR * SR

Where SR is stretch ratio
10   IV is polymer intrinsic viscosity
                in decalin at 135°C, dl/g
             C is polymer concentration in the gel, wt%
             T is stretch temp. °C
     The statistics of the regression were:
15   F ratio (6,95) = 118
             significance level = 99.9+%
             standard error of estimate = 3.0 g/d
        A comparison between the observed tenacities
and tenacities calculated from the regression equation
20   is shown in Figure 1.
        Figures 2 and 3 present response surface con-
tours for tenacity calculated from the regression equa-
tion on two important planes.
        In the experiments of Examples 3-99, a correl-
25   tion of modulus with spinning parameters was generally
parallel to that of tenacity. A plot of fiber modulus
versus tenacity is shown in Figure 4.
        It will be seen from the data, the regression
equations and the plots of the calculated and observed
30   results that the method of the invention enables sub-
stantial control to obtain desired fiber properties and
that greater controlability and flexibility is obtained
than by prior art methods.
        Further, it should be noted that many of the
35   fibers of these examples showed higher teancities and/or
modulus values than had been obtained by prior art
methods. In the prior art methods of Off. 30 04 699 and
GB 2051667, all fibers prepared had tenacities less than

3.0 GPa (35 g/d) and moduli less than 100 GPa (1181 g/d).
In the present instance, fiber examples Nos. 21, 67, 70,
73, 82, 84 and 88 exceeded both of these levels and
other fiber examples surpassed on one or the other
5   property.

In the prior art publications of Pennings and
coworkers, all fibers (prepared discontinuously) had
moduli less than 121 GPa (1372 g/d). In the present
instance continuous fiber examples No. 70, 71, 73, 82,
10 83, 84, 88 and 99 surpassed this level.

The fiber of example 71 was further tested for
resistance to creep at 23°C under a sustained load of
10% of the breaking load. Creep is defined as follows:

$$\% \text{ Creep} = 100 \times (A(s,t)-B(s))/B(s)$$

15 where B(s)   is the length of the test section
                  immediately after application of load

        A(s,t)   is the length of the test section at time
                  t after application of load, s

        A and B are both functions of the loads, while A
20   is also a function of time t.

For comparison, a commercial nylon tire cord (6 denier,
9.6 g/d tenacity) and a polyethylene fiber prepared in
accordance with Serial No. 225,288, filed January 15,
1981 by surface growth and subsequent hot stretching
25 (10 denier, 41.5 g/d tenacity) were similarly tested
for creep.

The results of these tests are presented in
Table II.

30

35

TABLE II

CREEP RESISTANCE AT 23°C

Load: 10% of Breaking Load

Time After Application of Load, Days	% Creep		
	Fiber of Example 71	Comparative Nylon Tire Cord	Surface Grown & Stretched Poly-ethylene
1	0.1	4.4	1.0
2	0.1	4.6	1.2
6	-	4.8	1.7
7	0.4	-	-
9	0.4	-	-
12	-	4.8	2.1
15	0.6	4.8	2.5
19	-	4.8	2.9
21	0.8	-	-
22	-	4.8	3.1
25	0.8	-	-
26	-	4.8	3.6
28	0.9	-	-
32	0.9	-	-
33	-	4.8	4.0
35	1.0	-	-
39	1.4	-	-
40	-	4.9	4.7
43	1.4	-	-
47	1.4	-	-
50	-	4.9	5.5
51	1.4	-	-
57	-	4.9	6.1
59	1.45	-	-

It will be seen that the fiber of example 71
showed 1.4% creep in 50 days at 23°C under the sustained
load equal to 10% of the breaking load. By way of
comparison, both the commercial nylon 6 tire cord and
the surface grown polyethylene fiber showed 5% creep
under similar test conditions.

The melting temperatures and the porosities
of the fibers of examples 64, 70 and 71 were determined.

Melting temperatures were measured using a DuPont 990 differential scanning calorimeter. Samples were heated in an argon atmosphere at the rate of 10°C/min. Additionally, the melting temperature was determined for the starting polyethylene powder from which the fibers of examples 64, 70 and 71 were prepared.

Porosities of the fibers were determined by measurements of their densities using the density gradient technique and comparison with the density of a compression molded plaque prepared from the same initial polyethylene powder. (The density of the compression molded plaque was 960 kg/m^3).

Porosity was calculated as follows:

$$\%, \text{Porosity} = \frac{960 - \text{fiber density, kg/m}^3}{960}$$

Results were as follows:

Sample	Melting Temp. °C	Fiber Density, Kg/m^3	Porosity,%
Polyethylene powder	138	--	--
Fiber of Example 64	149	982	0
Fiber of Example 70	149	976	0
Fiber of Example 71	150	951	1

The particular level and combination of properties exhibited by the fiber of examples 64, 70 and 71, i.e., tenacity at least 30 g/d, modulus in excess of 1000 g/d, work-to-break at least 7.5 GJ/m^3 and creep (at 23°C and 10% of breaking load) less than 3% in 50 days, melting temperature of at least 147°C and porosity less than 10% appears not to have been attained heretofore.

The following examples illustrate the effect of the second solvent upon fiber properties.

Examples 100-108

Fiber samples were prepared as described in Example 2, but with the following variations. The bottom discharge opening of the Helicone mixer was adapted to feed the polymer solution first to a gear pump and thence to a single hole conical spinning die. The cross-section of the spinning die tapered uniformly at a 7.5° angle from an entrance diameter of 10 mm to an exit

diameter of 1 mm. The gear pump speed was set to deliver 5.84 cm^3/min of polymer solution to the die. The extruded solution filament was quenched to a gel state by passage through a water bath located at a dis-

5 tance of 20 cm below the spinning die. The gel filament was wound up continuously on bobbins at the rate of 7.3 meters/min.

The bobbins of gel fiber were immersed in several different solvents at room temperature to

10 exchange with the paraffin oil as the liquid consti-
tuent of the gel. The solvents and their boiling points were:

Solvent	Boiling Point, °C
diethyl ether	34.5
n-pentane	36.1
methylene chloride	39.8
trichlorotrifluoroethane	47.5
n-hexane	68.7
carbon tetrachloride	76.8
n-heptane	98.4
dioxane	101.4
toluene	110.6

The solvent exchanged gel fibers were air dried at room temperature. Drying of the gel fibers was

25 accompanied in each case by substantial shrinkage of transverse dimensions. Surprisingly, it was observed that the shape and surface texture of the xerogel fibers departed progressively from a smooth cylindrical form in approximate proportion to the boiling point of the

30 second solvent. Thus, the fiber from which diethyl ether had been dried was substantially cylindrical whereas the fiber from which toluene had been dried was "C" shaped in cross-section.

The xerogel fibers prepared using TCTFE and

35 n-hexane as second solvents were further compared by stretching each at 130°C, incrementally increasing stretch ratio until fiber breakage occurred. The ten-sile properties of the resulting fibers were determined

as shown in Table III.

It will be seen that the xerogel fiber pre-
pared using TCTFE as the second solvent could be
stretched continuously to a stretch ratio of 49/1,
5 whereas the xerogel fiber prepared using n-hexane could
.be stretched continuously only to a stretch ratio of
33/1. At maximum stretch ratio, the stretched fiber
prepared using TCTFE second solvent was of 39.8 g/d
tenacity, 1580 g/d modulus and of 9.6 GJ/m^3 work-to-
10 break. This compares to 32.0 g/d tenacity, 1140 g/d
modulus and 8.4 GJ/m^3 obtained using n-hexane as the
second solvent.

TABLE III

Properties of Xerogel Fibers Stretched at 130°C

15   Feed Speed: 2.0 cm/min.

Example	Second Solvent	Stretch Ratio	Tenacity g/d	Modulus g/d	Elong. %	Work-to-break GJ/m³
100	TCTFE	16.0	23.3	740	5.0	6.5
101	TCTFE	21.8	29.4	850	4.5	8.1
102	TCTFE	32.1	35.9	1240	4.5	9.1
103	TCTFE	40.2	37.4	1540	3.9	9.2
104	TCTFE	49.3	39.8	1580	4.0	9.6
105	n-hexane	24.3	28.4	1080	4.8	8.0
106	n-hexane	26.5	29.9	920	5.0	9.4
107	n-hexane	32.0	31.9	1130	4.5	8.7
108	n-hexane	33.7	32.0	1140	4.5	8.4

Example 110

Following the procedures of Examples 3-99, an
8 wt% solution of isotactic polypropylene of 12.8
intrinsic viscosity (in decalin at 135°C), approximately
30 2.1 x 10^{6}M.W. was prepared in paraffin oil at 200°C. A
gel fiber was spun at 6.1 meters/min. The paraffin oil
was solvent exchanged with TCTFE and the gel fiber dried
at room temperature. The dried fiber was stretched 25/1
at a feed roll speed of 2 cm/min. Stretching was con-
35 ducted in a continuous manner for one hour at 160°C.

Fiber properties were as follows:

    denier - 105

    tenacity - 9.6 g/d

    modulus - 164 g/d

5   elongation - 11.5%

    work-to-break - 9280 in lbs/in^3

             (9.2 x 10^9 J/m^3 or 9.2 GJ/m^3

Examples 111-486

A series of xerogel fiber samples was prepared

10 as in Example 2 but using a gear pump to control melt flow rate. Variations were introduced in the following material and process parameters:

    a. polyethylene IV (molecular weight)

    b. polymer gel concentration

15   c. die exit diameter

    d. die included angle (conical orifice)

    e. spinning temperature

    f. melt flow rate

    g. distance to quench

20   h. gel fiber take-up velocity

    i. xerogel fiber denier

Each of the xerogel fiber samples prepared was stretched in a hot tube of 1.5 meter length blanketed with nitrogen and maintained at 100°C at the fiber inlet

25 and 140°C at the fiber outlet. Fiber feed speed into the hot tube was 4 cm/min. (Under these conditions the actual fiber temperature was within 1°C of the tube temperature at distances beyond 15 cm from the inlet). Each sample was stretched continuously at a series of

30 increasing stretch ratios. The independent variables for these experiments are summarized below:

Polymer Intrinsic Viscosity (dL/g)

11.5 - Examples 172-189, 237-241, 251-300, 339-371

15.5 - Examples 111-126, 138-140, 167-171, 204-236,

35   242-243, 372-449, 457-459

17.7 - Examples 127-137, 141-166, 190-203, 244-250,

         301-338

20.9 - Examples 450-456, 467-486

Gel Concentration

5% - Examples 127-137, 141-149, 167-171, 190-203,
244-260, 274-276, 291-306, 339-371

6% - Examples 111-126, 138-140, 204-236, 242-243,
372-418, 431-486

7% - Examples 150-166, 172-189, 237-241, 261-273,
277-290, 307-338

Die Diameter

Inches	Millimeters	
0.04	1	Examples 167-171, 237-241, 244-260, 274-276, 282-290, 301-306, 317-338, 366-371 and 460-466
0.08	2	Examples 111-166, 172-236, 242, 243, 261-273, 277-281, 291-300, 307-316, 339-365, 372-459 and 467-486.

Die Angle (Degrees)

0° - Examples 127-137, 141-149, 261-281, 307-316,
339-365, 419-430

7.5° - Examples 111-126, 138-140, 167-171, 204-243,
251-260, 301-306, 317-338, 372-418, 431-486

15° - Examples 150-166, 172-203, 244-250, 282-300,
366-371

Spinning Temperature

180°C - Examples 172-203, 237-241, 301-322, 339-371

200°C - Examples 111-126, 138-140, 167-171, 204-236,
242-243, 372-486

220°C - Examples 127-137, 141-166, 244-300, 232-338

Solution Flow Rate (cm^3/min)

2.92 ± 0.02 - Examples 116-122, 135-145, 150-152,
162-166, 172-173, 196-201, 214-222, 237,
240, 242-245, 251-255, 260-265, 277-284,
288-293, 301, 304-306, 310-312, 318-320,
347-360, 368-370, 372, 395-397, 401-407,
412-414, 419-424, 450-459, 467-481

4.37 ± 0.02 - Examples 204-208, 230-236, 377-379,
408-411

Solution Flow Rate (cm^3/min) (continued)

5.85 ± 0.05 — Examples 111-115, 123-134, 146-149,
153-161, 167-171, 180-195, 202-203,
209-213, 223-229, 238-239, 241, 256-259,
266-276, 285-287, 294-300, 302-303,
307-309, 315-317, 321-326, 335-338
361-367, 371, 373-376, 392-394, 398-400,
415-418, 431-433, 482-486

6.07 — Examples 339-346

8.76 — Examples 380-391

8.88 — Examples 246-250

11.71 ± 0.03 — Examples 434-437, 445-449

17.29 — Examples 438-440

Distance To Quench

Inches	Millimeters	Examples
5.5	140	116-126
6.0	152	127-137, 158-166, 172-173, 183-198, 222-229, 240-243, 246-259, 282-286, 293-296, 301, 302, 323-330, 366-368, 398-407, 419-430
6.5	165	268-273, 277-281
7.7	196	167-171
13.0	330	450-453
14.5	368	377-391
15.0	381	230-236, 408-411, 431-449, 454-456, 467-486
22.5	572	307-312, 339-349
23.6	600	111-115, 138-140
24.0	610	141-157, 174-182, 199-203, 209-221, 244-245, 287-292, 297-300, 303-306, 319-322, 331-338, 372, 392-394, 412-418, 460-466

Under all of the varied conditions, the take-up velocity varied from 90-1621 cm/min, the xerogel fiber denier from 98-1613, the stretch ratio from 5-174, the tenacity from 9-45 g/denier, the tensile

modulus from 218-1700 g/denier, the elongation from 2.5-29.4% and the Work-to-break from 1-27 GJ/m^3.

The results of each Example producing a fiber of at least 30 g/denier (2.5 GPa) tenacity or at least 1000 g/denier (85 GPa) modulus are displayed in Table IV.

TABLE IV
Stretched Fiber Properties

Example	Xerogel Fiber Denier	Stretch Ratio	Tenacity g/den	Modulus g/den	% Elong	Work-to Break (GJ/m^3)
113	1599.	50.	31.	1092.	4.0	12.
114	1599.	57.	34.	1356.	3.6	12.
115	1599.	72.	37.	1490.	3.5	13.
119	1837.	63.	35.	1257.	4.2	11.
122	1289.	37.	32.	988.	4.5	14.
126	440.	41.	31.	1051.	4.5	13.
128	1260.	28.	31.	816.	5.5	16.
130	1260.	33.	33.	981.	4.5	15.
131	1260.	43.	35.	1179.	4.0	14.
132	1260.	40.	37.	1261.	4.5	16.
133	1260.	39.	30.	983.	4.0	11.
134	1260.	53.	36.	1313.	4.0	13.
135	282.	26.	29.	1062.	3.5	10.
136	282.	26.	30.	1034.	3.5	1.
137	282.	37.	30.	1261.	3.5	10.
140	168.	23.	26.	1041.	3.5	9.
145	568.	40.	30.	1157.	4.0	12.
146	231.	21.	32.	763.	4.0	14.
147	231.	23.	36.	1175.	4.2	16.
148	231.	22.	33.	1131.	4.0	15.
149	231.	19.	31.	1090.	4.0	13.
151	273.	31.	28.	1117.	3.5	10.
157	1444.	64.	29.	1182.	3.0	10.
160	408.	35.	30.	1124.	4.0	12.
164	1385.	36.	32.	1210.	4.0	12.
166	1385.	39.	33.	1168.	4.0	12.
168	344.	26.	30.	721.	5.0	13.
169	344.	40.	32.	1188.	4.0	12.
170	344.	26.	30.	1060.	4.0	9.
171	344.	29.	31.	1172.	4.0	11.
179	1017.	68.	29.	1179.	4.0	11.
182	352.	65.	33.	1146.	3.7	13.
189	1958.	44.	27.	1050.	3.5	10.

-38-

TABLE IV (cont'd)

Stretched Fiber Properties

	Example	Xerogel Fiber Denier	Stretch Ratio	Tenacity g/den	Modulus g/den	% Elong	Work-to Break (GJ/m^3)
5	195	885.	59.	31.	1150.	4.0	11.
	201	496.	33.	29.	1082.	4.0	11.
	206	846.	37.	31.	955.	4.5	12.
	208	846.	63.	35.	1259.	3.5	13.
	212	368.	55.	39.	1428.	4.5	17.
10	213	368.	49.	35.	1311.	4.0	14.
	220	1200.	81.	34.	1069.	4.0	13.
	221	1200.	60.	30.	1001.	4.0	11.
	227	1607.	42.	30.	1050.	4.0	12.
	228	1607.	47.	30.	1114.	3.5	10.
15	229	1607.	53.	35.	1216.	4.0	13.
	233	1060.	34.	30.	914.	4.5	12.
	235	1060.	50.	37.	1279.	4.1	14.
	236	1060.	74.	45.	1541.	4.0	19.
	245	183.	23.	26.	1014.	4.0	11.
20	247	247.	16.	30.	1005.	4.5	14.
	248	247.	10.	30.	1100.	4.0	11.
	249	247.	11.	31.	1132.	4.0	12.
	250	247.	19.	37.	1465.	3.8	15.
	251	165.	34.	31.	1032.	4.5	13.
25	252	165.	33.	31.	998.	4.5	13.
	254	165.	41.	31.	1116.	4.0	11.
	255	165.	40.	29.	1115.	4.0	10.
	272	1200.	41.	24.	1122.	3.0	8.
	273	1200.	64.	27.	1261.	2.5	7.
30	274	154.	27.	30.	854.	4.5	13.
	275	154.	44.	32.	1063.	4.5	12.
	276	154.	38.	30.	1054.	4.0	10.
	280	291.	39.	30.	978.	4.0	12.
	281	291.	43.	29.	1072.	4.0	11.
35	284	254.	30.	32.	1099.	4.5	14.
	308	985.	27.	30.	900.	4.3	12.
	309	985.	34.	35.	1210.	3.8	12.
	311	306.	30.	31.	990.	4.4	14.

TABLE IV (cont'd)

Stretched Fiber Properties

	Example	Xerogel Fiber Denier	Stretch Ratio	Tenacity g/den	Modulus g/den	% Elong	Work-to Break (GJ/m³)
5	312	306.	30.	32.	1045.	4.0	15.
	314	1234.	45.	37.	1320.	4.0	12.
	315	344.	25.	30.	970.	4.0	11.
	317	254.	29.	32.	1270.	3.5	11.
	320	190.	29.	30.	1060.	4.0	12.
10	322	307.	25.	29.	1030.	4.0	11.
	323	340.	25.	34.	1293.	4.1	15.
	324	340.	23.	33.	996.	4.4	14.
	325	340.	30.	37.	1241.	4.1	15.
	326	340.	35.	39.	1480.	3.7	14.
15	327	373.	24.	30.	920.	4.5	14.
	328	373.	27.	34.	1080.	4.5	16.
	329	373.	30.	36.	1349.	4.0	14.
	330	373.	35.	37.	1377.	3.9	14.
	332	218.	34.	35.	1320.	3.9	14.
20	333	218.	30.	37.	1364.	4.0	16.
	334	218.	30.	31.	1172.	3.9	12.
	335	326.	26.	37.	1260.	4.5	16.
	336	326.	30.	39.	1387.	4.2	16.
	337	326.	42.	42.	1454.	4.0	18.
25	338	326.	42.	37.	1440.	3.9	15.
	339	349.	55.	29.	1330.	3.3	9.
	345	349.	31.	29.	1007.	4.5	14.
	346	349.	51.	34.	1165.	4.3	14.
	357	772.	45.	31.	990.	4.4	16.
30	358	772.	51.	27.	1356.	3.0	11.
	359	772.	58.	32.	1240.	3.7	12.
	360	772.	59.	33.	1223.	3.8	13.
	364	293.	47.	38.	1407.	4.5	17.
	375	1613.	50.	30.	960.	4.1	11.
35	379	791.	46.	32.	1110.	3.9	12.
	382	1056.	68.	34.	1280.	3.7	12.
	383	921.	51.	31.	1090.	4.0	14.
	386	1057.	89.	34.	1250.	3.8	13.

-40-

TABLE IV (cont'd)

Stretched Fiber Properties

	Example	Xerogel Fiber Denier	Stretch Ratio	Tenacity g/den	Modulus g/den	% Elong	Work-to Break (GJ/m^3)
5	387	984.	59.	33.	1010.	4.3	14.
	394	230.	29.	31.	982.	4.3	13.
	400	427.	32.	30.	970.	4.1	12.
	405	1585.	39.	33.	1124.	3.6	24.
	407	1585.	174.	32.	1040.	4.0	13.
10	418	1370.	51.	33.	1160.	3.7	11.
	419	344.	23.	30.	1170.	3.8	11.
	421	1193.	30.	31.	880.	4.6	14.
	422	1193.	39.	35.	1220.	3.9	13.
	423	1193.	51.	34.	1310.	3.4	11.
15	424	1193.	50.	36.	1390.	3.6	13.
	426	1315.	32.	30.	860.	4.4	12.
	427	1315.	42.	33.	1160.	3.9	13.
	428	1315.	46.	34.	1170.	3.8	13.
	429	395.	19.	35.	840.	4.5	12.
20	430	395.	25.	31.	1100.	3.9	13.
	435	1455.	36.	31.	920.	4.3	12.
	436	1455.	43.	31.	1120.	3.6	11.
	437	1455.	51.	33.	1060.	3.3	11.
	440	1316.	37.	32.	1130.	4.0	13.
25	441	453.	31.	32.	990.	4.7	14.
	442	453.	49.	39.	1320.	4.4	18.
	443	453.	34.	33.	1060.	4.4	13.
	444	453.	55.	36.	1410.	3.6	14.
	446	402.	28.	30.	1107.	4.0	11.
30	447	402.	22.	30.	870.	5.0	14.
	448	402.	34.	36.	1175.	4.3	8.
	449	402.	38.	37.	1256.	4.3	15.
	451	461.	33.	33.	1070.	4.4	14.
	452	461.	38.	35.	1130.	4.1	13.
35	453	461.	40.	35.	1220.	3.7	12.
	454	64.	14.	34.	1080.	4.7	13.
	455	64.	17.	35.	1263.	3.4	11.
	456	64.	26.	40.	1453.	3.8	12.

TABLE IV (cont'd)

		Xerogel Fiber	Stretch	Stretched Fiber Properties			
	Example	Denier	Ratio	Tenacity g/den	Modulus g/den	% Elong	Work-to Break (GJ/m^3)
5	460	268.	32.	35.	1220.	4.3	15.
	462	268.	29.	34.	1100.	4.2	14.
	463	268.	32.	34.	1110.	4.1	16.
	464	268.	43.	40.	1390.	3.9	15.
	465	420.	53.	41.	1550.	3.7	16.
10	466	420.	27.	31.	1010.	4.0	12.
	467	371.	24.	31.	960.	4.4	13.
	468	371.	63.	45.	1560.	3.9	17.
	470	1254.	40.	35.	1100.	4.1	13.
	471	1254.	43.	37.	1190.	4.0	14.
15	472	1254.	45.	38.	1320.	4.0	14.
	473	1254.	66.	39.	1600.	3.5	13.
	474	210.	44.	43.	1700.	3.5	15.
	475	210.	21.	34.	1170.	4.0	12.
	476	210.	27.	38.	1420.	3.6	14.
20	479	1227.	50.	34.	1180.	4.1	14.
	480	1227.	48.	33.	1140.	4.1	13.
	481	1227.	44.	35.	1230.	4.1	14.
	483	1294.	29.	31.	1000.	4.3	13.
	484	1294.	42.	36.	1350.	3.7	14.
25	485	340.	26.	32.	1160.	3.8	11.
	486	340.	18.	27.	1020.	4.1	11.

In order to determine the relationships of the fiber properties to the process and material parameters, all of the data from Example 111-486, including those

30 Examples listed in Table IV, were subjected to statistical analysis by multiple linear regression. The regression equation obtained for fiber tenacity was as follows: Tenacity, g/d =11.88 + 2.221IV' + 1.147C' + 1.948TM' +0.822Q' -1.167L' -2.438DO' +0.532SR

35   -0.726IV'DA' +1.399IV'TM' +0.534 IV'L' +0.046IV'SR -0.754C'DA' -0.391C'Q' -0.419C'DO' -1.327D'TM' +0.366D'L' -0.577DA'TM'

$$-0.790 \, DA'Q' \, -0.034 \, DA'SR \, -0.049 \, TM'SR$$
$$+0.809 \, Q'L' \, -0.313 \, Q'DO' \, - \, 0.334 \, (IV')^2$$
$$+0.115 \, (L')^2 \, +0.564 \, (DO')^2 \, -0.00237 \, (SR)^2$$

where:

IV' = (polymer IV, dL/g-14.4)/3.1

C' = Gel concentration, % - 6

TM' = (spinning temp.°C - 200)/20

Q' = (spin flow rate, cc/min - 4.38)/1.46

L' = (distance to quench, in - 15)/9

DO' = 1.4427 log (xerogel fiber denier/500)

SR = stretch ratio

(xerogel fiber denier/stretched fiber denier)

DA' = (die angle,° - 7.5)/7.5

D' = (die exit diameter, inches - 0.06)/0.02

The statistics of the reggression were;

F ratio (26, 346) = 69

Significance Level = 99.9 +%

Standard error of estimate = 2.6 g/denier

In the vicinity of the center of the experimental space these effects may be summarized by considering the magnitude of change in the factor which is required to increase tenacity of 1 g/d. This is given below.

Factor	Factor Change Required to Increase Tenacity By 1 g/denier	
IV	+1	dL/g
Conc.	+1	wt%
Spin Temp.	+10	°C
Spin Rate	±(saddle)	cc/min
Die Diam.	-0.010	inches
Die Angle	-2	degrees
Dist. to Quench	-4	inches
Xerogel Fiber Denier	-25	
Stretch Ratio	+2/1	

High fiber tenacity was favored by increasing polymer IV, increasing gel concentration, increasing spinning temperature, decreasing die diameter, decreasing distance to quench, decreasing xerogel fiber dia-

meter, increasing stretch ratio and 0° die angle (straight capillary).

It will be seen that the method of the invention enables substantial control to obtain desired fiber properties and that greater controlability and flexability is obtained than by prior art methods.

In these experiments, the effects of process parameters upon fiber modulus generally paralled the effects of these variables upon tenacity. Fiber modulus was correlated with tenacity as follows

$$\text{modulus, g/d} = 42(\text{tenacity, g/d}) - 258$$

Significance of the correlation between modulus and tenacity was 99.99 +%. Standard error of the estimate of modulus was 107 g/d.

It should be noted that many of the fibers of these examples show higher tenacities and/or higher modulus than had seen obtained by prior art methods.

The densities and porosities of several of the xerogel and stretched fibers were determined.

	Xerogel fiber		Stretched fiber	
Example	Density kg/m^3	% Porosity	Density, kg/m^3	% Porosity
115	934	2.7	--	--
122	958	0.2	0.965	0
126	958	0.2	--	--
182	906	5.6	940	2.1

The porosities of these samples were substantially lower than in the prior art methods cited earlier.

EXAMPLES 487-583

In the following examples of multi-filament spinning and stretching, polymer solutions were prepared as in Example 2. The solutions were spun through a 16 hole spinning die using a gear pump to control solution flow rate. The aperatures of the spinning die were straight capillaries of length-to-diameter ratio of 25/1. Each capillary was preceded by a conical entry region of 60° included angle.

The multi-filament solution yarns were quenched to a gel state by passing through a water bath

-44-

located at a short distance below the spinning die. The gel yarns were wound up on perforated dye tubes.

EXAMPLES 487-495

ONE STAGE "DRY STRETCHING" OF MULTI-FILAMENT YARN

5   The wound tubes of gel yarn were extracted with TCTFE in a large Sohxlet apparatus to exchange this solvent for paraffin oil as the liquid constituent of the gel. The gel fiber was unwound from the tubes and the TCTFE solvent was evaporated at room tempera-
10   ture.

        The dried xerogel yarns were stretched by passing the yarn over a slow speed feed godet and idler roll through a hot tube blanketed with nitrogen, onto a second godet and idler roll driven at a higher speed.
15   The stretched yarn was collected on a winder.

        It was noted that some stretching of the yarn (approximately 2/1) occurred as it departed the feed godet and before it entered the hot tube. The overall stretch ratio, i.e., the ratio of the surface speeds of
20   the godets, is given below.

        In examples 487-495, the diameter of each hole of the 16 filament spinning die was 0.040 inch (one millimeter) the spinning temperature was 220°C, the stretch temperature (in the hot tube) was 140°C and the
25   feed roll speed during stretching was 4 cm/min. In examples 487-490 the polymer IV was 17.5 and the gel concentration was 7 weight %. In examples 491-495 the polymer IV was 22.6. The gel concentration was 9 weight % in example 491, 8 weight % in examples 492-493 and 6
30   weight % in examples 494 and 495. The distance from the die face to the quench bath was 3 inches (7.52 cm) in examples 487, 488, 494 and 495 and 6 inches (15.2 cm) in examples 490-493. The other spinning conditions and the properties of the final yarns were as follows:

35

Yarn Properties

Ex. No.	Spin Rate cc/min- fil	Gel Fiber Take-up Speed cc/min	SR	Denier	Ten g/d	Mod g/d	% Elong	W-t-B GJ/m3
487	1.67	1176	35	41	36	1570	3.3	13
488	2.86	491	25	136	27	1098	3.7	10
489	2.02	337	25	132	29	1062	3.6	10
490	2.02	337	30	126	31	1275	3.5	11
491	1.98	162	25	151	33	1604	3.0	11
492	1.94	225	25	227	29	1231	3.3	11
493	1.94	225	30	143	34	1406	3.3	12
494	1.99	303	30	129	34	1319	3.4	12
495	1.99	303	35	112	35	1499	3.2	13

EXAMPLES 496-501

ONE STAGE "WET STRETCHING" OF MULTI-FILAMENT YARN

The wound gel yarns still containing the paraffin oil were stretched by passing the yarn over a slow speed feed godet and idler roll through a hot tube blanketed with nitrogen onto a second godet and idler roll driven at high speed. It was noted that some stretching of the yarn (approximately 2/1) occurred as it departed the feed godet and before it entered the hot tube. The overall stretch ratio, i.e., the ratio of the surface speeds of the godets is given below. The stretching caused essentially no evaporation of the paraffin oil (the vapor pressure of the paraffin oil is 0.001 atmospheres at 149°C). However, half of the paraffin oil content of the gel yarns was exuded during stretching. The stretched gel yarns were extracted with TCTFE in a Sohxlet apparatus, then unwound and dried at room temperature.

In each of the examples 496-501 the spinning temperatures was 220°C, the gel concentration was 6 weight % the distance from the spinning die to the water quench was 3 inches (7.6 cm).

In examples 496 and 499-501 the diameter of each hole of the spinning die was 0.040 inches (0.1 cm). In examples 497 and 498 the hole diameters were 0.030

-46-

inches (0.075 cm). In examples 496 and 494-501 the
polymer IV was 17.5. In examples 497 and 498 the poly-
mer IV was 22.6. The other spinning conditions and
properties of the final yarns were as follows:

Ex. No.	Spinning Rate cc/min-fil	Gel Fiber Take-up Speed cm/min	Stretch Temp	Stretch Ratio	Denier
496	2.02	313	140	22	206
497	1.00	310	140	12.5	136
498	1.00	310	140	15	94
499	2.02	313	120	20	215
500	2.02	313	120	22.5	192
501	2.02	313	120	20	203

Ex. No.	Tenacity g/d	Modulus g/d	% Elong	Work-to-Break GJ/m^3
496	25	1022	3.7	9
497	28	1041	3.6	9
498	32	1389	2.8	9
499	30	1108	4.5	14
500	30	1163	4.2	13
501	27	1008	4.2	11

EXAMPLES 502-533

In the following examples a comparison is made
between alternative two stage modes of stretching the
same initial batch of yarn. All stretching was done in
a hot tube blanketed with nitrogen.

Example 502

GEL YARN PREPARATION

The gel yarn was prepared from a 6 weight %
solution of 22.6 IV polyethylene as in example 2. The
yarn was spun using a 16 hole x 0.030 inch (0.075 cm)
die. Spinning temperature was 220°C. Spin rate was 1
cm^3/min-fil. Distance from the die face to the quench
bath was 3 inches (7.6 cm). Take-up speed was 308 cm/
min. Nine rolls of 16 filament gel yarn was prepared.

Examples 503-576

"WET-WET" STRETCHING

In this mode the gel yarn containing the
paraffin oil was stretched twice. In the first stage,

three of the rolls of 16 filament gel yarns described
in example 502 above were combined and stretched
together to prepare a 48 filament stretched gel yarn.
The first stage stretching conditions were: Stretch
temperature 120°C, feed speed 35 cm/min, stretch ratio
12/1. A small sample of the first stage stretched gel
yarn was at this point extracted with TCTFE, dried and
tested for tensile properties. The results are given
below as example 503.

The remainder of the first stage stretched
gel yarn was restretched at 1 m/min feed speed. Other
second stage stretching conditions and physical proper-
ties of the stretched yarns are given below.

Ex. No.	2nd Stage Stretch Temp - °C	2nd Stage Stretch Ratio	Denier	Tenacity g/d
503	---	---	504	22
504	130	1.5	320	28
505	130	1.75	284	29
506	130	2.0	242	33
507	140	1.5	303	31
508	140	1.75	285	32
509	140	2.25	222	31
510	145	1.75	285	31
511	145	2.0	226	32
512	145	2.25	205	31
513	150	1.5	310	28
514	150	1.7	282	28
515	150	2.0	225	33
516	150	2.25	212	31

Ex. No.	Modulus g/d	% Elong	Work-to-Break GJ/m³	Melting* Temp, °C
503	614	5.5	12	147
504	1259	2.9	8	---
505	1396	2.6	8	150,157
506	1423	2.8	9	---
507	1280	3.1	9	---
508	1367	3.0	9	149,155
509	1577	2.6	8	---
510	1357	3.0	9	---
511	1615	2.7	8	---
512	1583	2.5	8	151,156
513	1046	3.0	9	---
514	1254	2.9	8	---
515	1436	2.9	9	---
516	1621	2.6	8	152,160

*The unstretched xerogel melted at 138°C.

The density of the fiber of example 515 was determined to be 980 kg/m³. The density of the fiber was therefore higher than the density of a compression molded plaque and the porosity was essentially zero.

EXAMPLES 517-522

"WET-DRY" STRETCHING

In this mode the gel yarn was stretched once then extracted with TCTFE, dried and stretched again.

In the first stage, three of the rolls of 16 filament gel yarn described in Example 502 were combined and stretched together to prepare a 48 filament stretched gel yarn. The first stage stretching conditions were: stretch temperature 120°C, feed speed 35 cm/min, stretch ratio 12/1.

The first stage stretched gel yarn was extracted with TCTFE in a Sohxlet apparatus, rewound and air dried at room temperature, then subjected to a second stage of stretching in the dry state at a feed speed of 1 m/min. Other second stage stretching conditions and physical properties of the stretched yarn are given below.

Example	2nd Stage Stretch Temp, °C	2nd Stage Stretch Ratio	Denier	Ten g/d	Mod g/d	% Elong.	W-t-B$_3$ GJ/m	Melt Temp, °C
517	130	1.25	390	22	1193	3.0	7	—
518	130	1.5	332	26	1279	2.9	7	150,157
519	140	1.5	328	26	1291	3.0	8	—
520	140	1.75	303	27	1239	2.7	8	150,159
521	150	1.75	292	31	1427	3.0	9	—
522	150	2.0	246	31	1632	2.6	8	152,158

EXAMPLES 523-533

"DRY-DRY" STRETCHING

In this mode the gel yarn described in example 502 was extracted with TCTFE, dried, then stretched in two stages. In the first stage, three of the rolls of 16 filament yarn were combined and stretched together to prepare a 48 filament stretched xerogel yarn. The first stage stretching conditions were: stretch temperature 120°C, feed speed 35 cm/min., stretch ratio 10/1. The properties of the first stage stretched xerogel yarn are given as example 523 below. In the second stretch stage the feed speed was 1 m/min. Other second stage stretching conditions and physical properties of the stretched yarns are given below.

Example	Stretch Temp, °C	SR	Denier	Ten g/d	Mod g/d	% Elong.	W-t-B$_3$ GJ/m	Melt Temp, °C
523	–	–	392	21	564	4.3	9	146, 153
524	130	1.5	387	24	915	3.1	7	–
525	130	1.75	325	23	1048	2.4	6	150, 158
526	140	1.5	306	28	1158	2.9	8	–
527	140	1.75	311	28	1129	2.9	8	–
528	140	2.0	286	24	1217	2.3	6	150, 157
529	150	1.5	366	26	917	3.3	8	–
530	150	1.75	300	28	1170	3.0	8	–
531	150	2.0	273	31	1338	3.8	8	–
532	150	2.25	200	32	1410	2.2	8	–
533	150	2.5	216	33	1514	2.5	8	152, 156

The density of the fiber of example 529 was determined to be 940 Kg/m^3. The porosity of the fiber

was therefore 2%.

EXAMPLES 534-542

MULTI-STAGE STRETCHING OF MULTI-FILAMENT YARN

In the following examples a comparison is made between two elevated temperature stretches and a three stage stretch with the first stage at room temperature. The same initial batch of polymer solution was used in these examples.

EXAMPLE 534

UNSTRETCHED GEL YARN PREPARATION

A 6 weight % solution of 22.6 IV polyethylene yarn was prepared as in example 2. A 16 filament yarn was spun and wound as in example 502.

EXAMPLE 535

PREPARATION OF GEL YARN STRETCHED AT ROOM TEMPERATURE

The unstretched gel yarn prepared as in example 534 was led continuously from a first godet which set the spinning take-up speed to a second godet operating at a surface speed of 616 cm/min. In examples 540-542 only, the as-spun gel fiber was stretched 2/1 at room temperature in-line with spinning. The once stretched gel fiber was wound on tubes.

EXAMPLES 536-542

The 16 filament gel yarns prepared in examples 534 and 535 were stretched twice at elevated temperature. In the first of such operations the gel yarns were fed at 35 cm/min to a hot tube blanketed with nitrogen and maintained at 120°C. In the second stage of elevated temperature stretching the gel yarns were fed at 1 m/min and were stretched at 150°C. Other stretching conditions and yarn properties are given below.

Example	SR RT	SR 120°C	SR 150°C	Total SR	Denier	Ten g/den	Mod g/den	Elong	W-t-B GJ/m^3
536	-	8.3	2.25	18.7	128	23	1510	2.6	6
537	-	8.3	2.5	20.8	116	30	1630	3.0	9
538	-	8.3	2.75	22.8	108	30	1750	2.7	8
539	-	8.3	3.0	24.9	107	31	1713	2.6	8
540	2	6.8	2.0	27.2	95	30	1742	2.5	7
541	2	6.8	2.25	30.6	84	34	1911	2.5	8
542	2	6.8	2.5	34	75	32	1891	2.2	7

EXAMPLES 543-551

POLYETHYLENE YARNS OF EXTREME MODULUS

The highest experimental value reported for the modulus of a polyethylene fiber appears to be by P.

5   J. Barham and A. Keller, J. Poly. Sci., Polymer Letters ed. 17, 591 (1979). The measurement 140 GPa (1587 g/d) was made by a dynamic method at 2.5 Hz and 0.06% strain and is expected to be higher than would be a similar measurement made by A.S.T.M. Method D2101 "Tensile

10 Properties of Single Man Made Fibers Taken from Yarns and Tows" or by A.S.T.M. Method D2256 "Breaking Load (Strength) and Elongation of Yarn by the Single Strand Method." The latter methods were used in obtaining the data reported here.

15   The following examples illustrate the preparation of novel polyethylene yarns of modulus exceeding 1600 g/d and in some cases of modulus exceeding 2000 g/d. Such polyethylene fibers and yarns were heretofore unknown. In the following examples all yarns were made

20 from a 22.6 IV polyethylene, 6 weight % solution prepared as in example 2 and spun as in example 502. All yarns were stretched in two stages. The first stage stretch was at a temperature of 120°C. The second stage stretch was at a temperature of 150°C. Several 16

25 filament yarn ends may have been combined during stretching. Stretching conditions and yarn properties are given below.

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Example	Feed-1 cm/min	SR-1	Feed-2 cm/min	SR-2	Fils	Ten g/den	Mod g/den	Elong	W-t-B GJ/m^3
			Wet-Wet						
543	25	15	100	2.25	48	39	1843	2.9	-
544	35	12.5	100	2.5	64	31	1952	2.6	8
545	35	10.5	100	2.75	48	31	1789	2.4	9
546	100	6.4	200	2.85	48	27	1662	2.5	8
			Wet-Dry						
547	25	15	100	2.0	48	36	2109	2.5	13
548	25	15	100	2.0	48	32	2305	2.5	9
549	25	15	100	2.0	48	30	2259	2.3	8
550	25	15	100	1.87	48	35	2030	2.7	11
551	25	15	100	1.95	16	35	1953	3.0	8

The yarns of examples 548 and 550 were characterized by DTA and density measurement. The results, displayed below, indicate two distinct peaks at the melting points indicated, quite unlike the broad single peak at 145.5°C or less reported by Smith and Lemstra in J. Mat. Sci., vol 15, 505 (1980).

Example	Melt Temp(s)	Density	% Porosity
548	147,155°C	977 kg/m^3	0
550	149,156°C	981 kg/m^3	0

EXAMPLES 552-558

POLYPROPYLENE YARNS OF EXTREME MODULUS

The highest reported experimental value for the modulus of a polypropylene material (fiber or other form) appears to be by T. Williams, T. Mat. Sci., 6, 537 (1971). Their value on a solid state extruded billet was 16.7 GPa (210 g/d). The following examples illustrate the preparation of polypropylene continuous fibers with modulus exceeding 220 g/d and in some cases of modulus exceeding 250 g/d.

In the following examples all fibers were made from an 18 IV polypropylene, 6 weight % solution in paraffin oil prepared as in example 2. In Examples 552-556, the fibers were spun with a single hole conical die of 0.040" (0.1 cm) exit diameter and 7.5% angle.

Solution temperature was 220°C. A melt pump was used to control solution flow rate at 2.92 cm^3/min. Distance from the die face to the water quench was 3 inches (7.6 cm). The gel fibers were one stage wet stretched at 25 cm/min feed roll speed into a 1.5 m hot tube blanketed with nitrogen. The stretched fibers were extracted in TCTFE and air dried. Other spinning and stretching conditions as well as fiber properties are given below.

Example	Gel Fiber Stretch Take-up Speed	Temp °C	SR	Denier	Ten g/d	Mod g/d	Elong	W-t-B GJ/m^3
552	432	139	10	33	13.0	298	15.8	21
553	432	138	10	34	13.0	259	18.3	25
554	317	140	5	45	11.2	262	19.9	20
555	317	140	10	51	11.0	220	19.6	22
556	317	150	10	61	8.8	220	29.8	29

The fiber of example 556 was determined by DTA to have a first melting temperature of 170-171°C with higher order melting temperatures of 173°C, 179°C and 185°C. This compares with the 166°C melting point of the initial polymer. The moduli of these fibers substantially exceed the highest previously reported values.

In Examples 557 and 558, the yarns were spun with a 16 hole x 0.040 inch (1 mm) capillary die. The solution temperature was 223°C, and the spinning rate was 2.5 cm^3/min-filament. The distance from the die face to the water quench bath was 3 inches (7.6 cm). Take-up speed was 430 cm/min. The gel yarns were "wet-wet" stretched in two stages. The first stage stretching was at 140°C at a feed speed of 35 cm/min. The second stage stretching was at a temperature of 169°C, a feed speed of 100 cm/min and a stretch ratio of 1.25/1. Other stretching conditions as well as fiber properties are given below.

-54-

Example	SR-1	Denier	Ten g/den	Mod g/den	% Elong.	W-t-B GJ/M^3
557	9.5	477	10	368	6.8	14
558	9.0	405	10	376	5.7	13

The moduli of these yarns very substantially exceed the highest previously reported values.

Claims:

1. A process for producing a high strength, high modulus shaped thermoplastic article of substantially indefinite length which comprises the steps:

5   a) forming a solution of a thermoplastic crystalline polymer selected from the group consisting of polyethylene, polypropylene, polyoxymethylene, poly-butene-1, poly(vinylidene fluoride) and poly(4-methyl-pentene-1) in a first, nonvolatile solvent at a first

10   concentration by weight of polymer per unit weight of first solvent, said thermoplastic polymer having a weight average molecular length between 7×10^4 and 71×10^4 backbone atoms and the solubility of said thermoplastic polymer in said first solvent at a first

15   temperature being at least said first concentration;

b) extruding said solution through an aperture, said solution being at a temperature no less than said first temperature upstream of the aperture and being substantially at the first concentration both

20   upstream and downstream of the aperture;

c) cooling the solution adjacent to and downstream of the aperture to a second temperature below the temperature at which a rubbery gel is formed, forming a gel containing first solvent of substantially

25   indefinite length;

d) extracting the gel containing first solvent with a second, volatile solvent for a sufficient contact time to form a gel containing second solvent which gel is substantially free of first solvent and is

30   of substantially indefinite length;

e) drying the gel containing second solvent to form a xerogel of substantially indefinite length free of first and second solvent; and

f) stretching at least one of:

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                (i) the gel containing the first solvent,
                (ii) the gel containing the second solvent
                     and,

(iii) the xerogel, at a total stretch
ratio:

(i) in the case of polyethylene which is
sufficient to achieve a tenacity of at least 20 g/denier
and a modulus of at least 600 g/denier,

(ii) in the case of polypropylene which is
sufficient to achieve a tenacity of at least 10 g/denier
and a modulus of at least 180 g/denier, and

(iii) in the case of polyoxymethylene,
polybutene-1, poly(vinylidene fluoride) or poly
(4-methylpentene-1) of at least 10:1.

2. The process of claim 1 wherein said aper-
ture has an essentially circular cross-section; said gel
containing first solvent and gel containing second sol-
vent are each gel fibers; said xerogel is a xerogel
fiber; and said thermoplastic article is a fiber.

3. The process of claim 1 or 2 wherein said
first temperature is between 150°C and 250°C; said
second temperature is between -40°C and 40°C; the cool-
ing rate between said first temperature and said second
temperature is at least 50°C/min; and said first solvent
is a hydrocarbon.

4. The process of any previous claim wherein
said first solvent has a vapor pressure less than 20 kPa
at said first temperature and said second solvent is
non-flammable and has an atmospheric boiling point less
than 80°C.

5. The process of any previous claim wherein
said second solvent has an atmospheric boiling point
less than 50°C.

6. The process of any previous claim wherein
said stretching step (f) is conducted in at least two
stages.

7. The process of any previous claim wherein
the thermoplastic crystalline polymer is polyethylene
and at least a portion of stretching is performed at a
temperature between 120°C and 160°C.

8. The process of claim 7 wherein the

stretching is performed in at least two stages with the latest stage performed at a temperature of between 135°C and 150°C.

9. A polyethylene fiber of substantially indefinite length being of weight average molecular weight at least 500,000 and having a tenacity of at least 20 g/denier, a tensile modulus at least 500 g/denier, a creep value no more than 5% (when measured at 10% of breaking load for 50 days at 23°C), a porosity less than 10% and a melting temperature of at least 147°C.

10. The polyethylene fiber of claim 9 having a tenacity of at least 30 g/denier and a tensile modulus of at least 1000 g/denier.

11. The polyethylene fiber of claim 9 or 10 having a tensile modulus of at least 1600 g/denier.

12. The polyethylene fiber of claim 11 having a tensile modulus of at least 2000 g/denier.

13. The polyethylene fiber of claim 9 or 10 or 11 or 12 being of weight average molecular weight between 2,000,000 and 8,000,000.

14. A polyethylene fiber of substantially indefinite length being of weight average molecular weight of at least 1,000,000 and having a tensile modulus of at least 1600 g/denier, a melting point of at least 147°C and an elongation-to-break of not more than 5%.

15. A polypropylene fiber of substantially indefinite length being of weight average molecular weight of at least 750,000 and having a tenacity of at least 8 g/denier, a tensile modulus of at least 160 g/denier and a melting temperature of at least 168°C.

16. The polypropylene fiber of claim 15 having a tensile modulus of at least 220 g/denier.

17. The polypropylene fiber of claim 15 or 16 being of weight average molecular weight between 2,000,000 and 8,000,000.

18. A polyolefin gel fiber of substantially

indefinite length comprising between 4 and 20 weight %
solid polyethylene of weight average molecular weight at
least 500,000 or solid polypropylene of weight average
molecular weight at least 750,000, and between 80 and 96
5   weight % of a swelling solvent miscible with a high
boiling hydrocarbon and having an atmospheric boiling
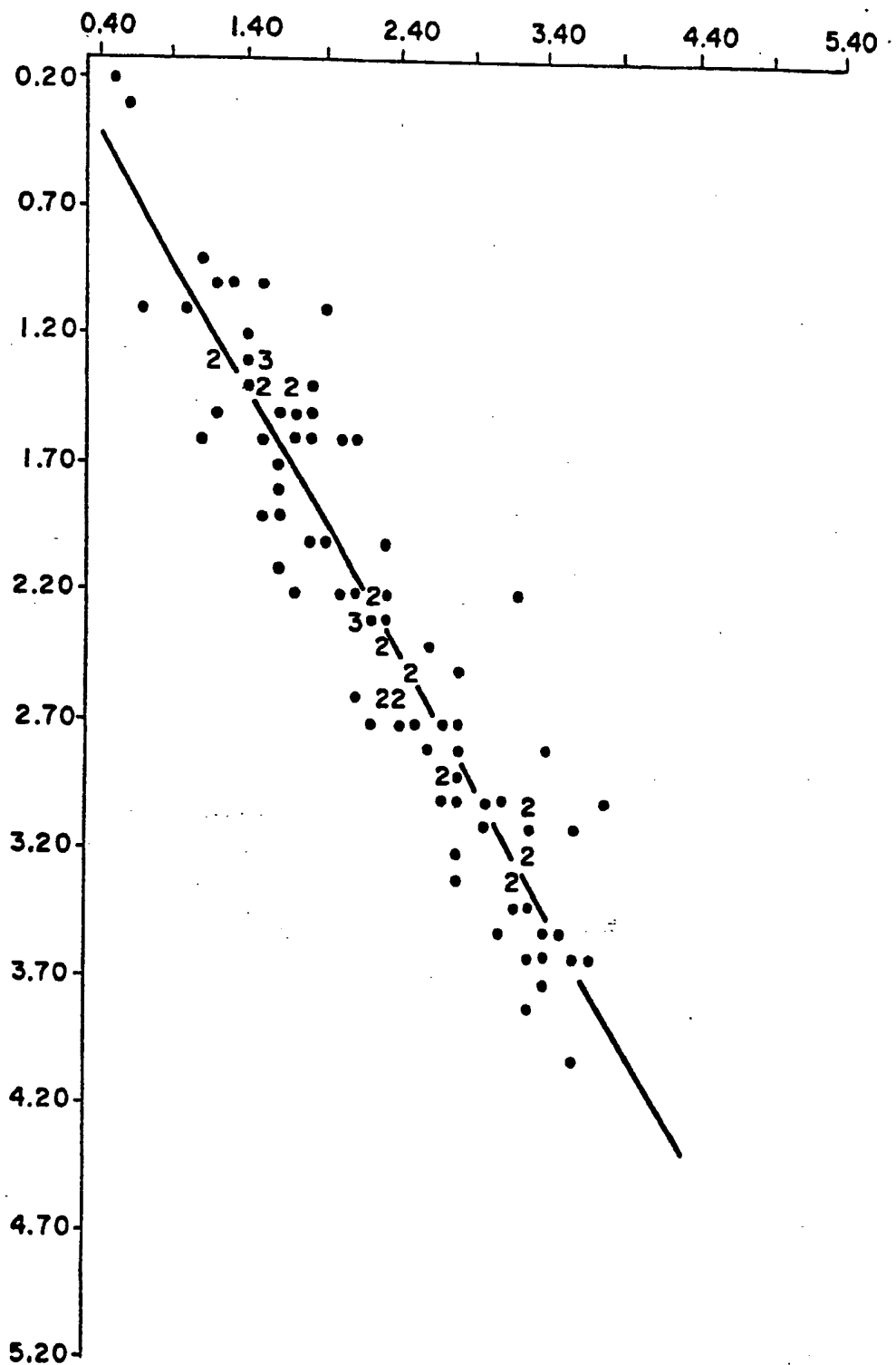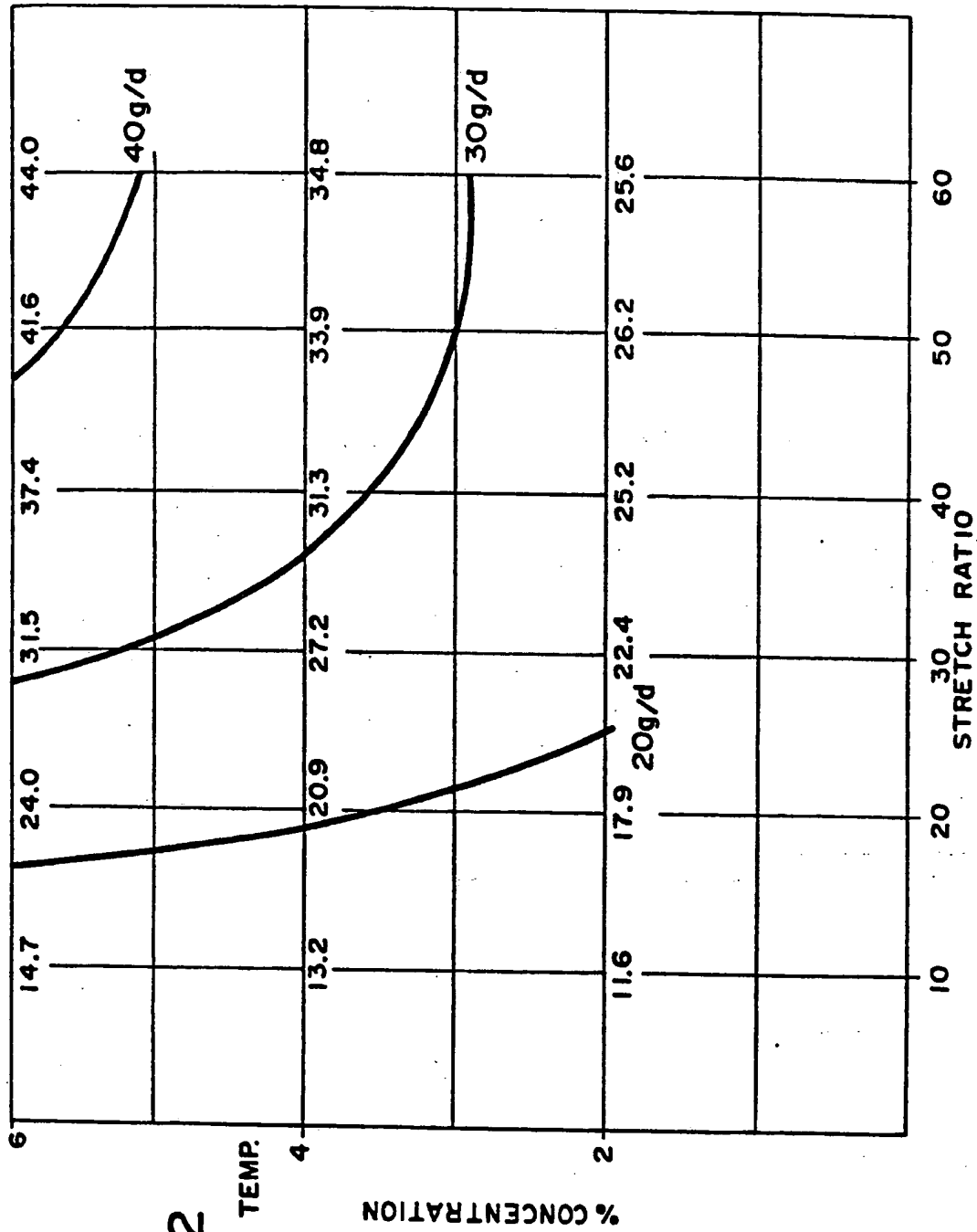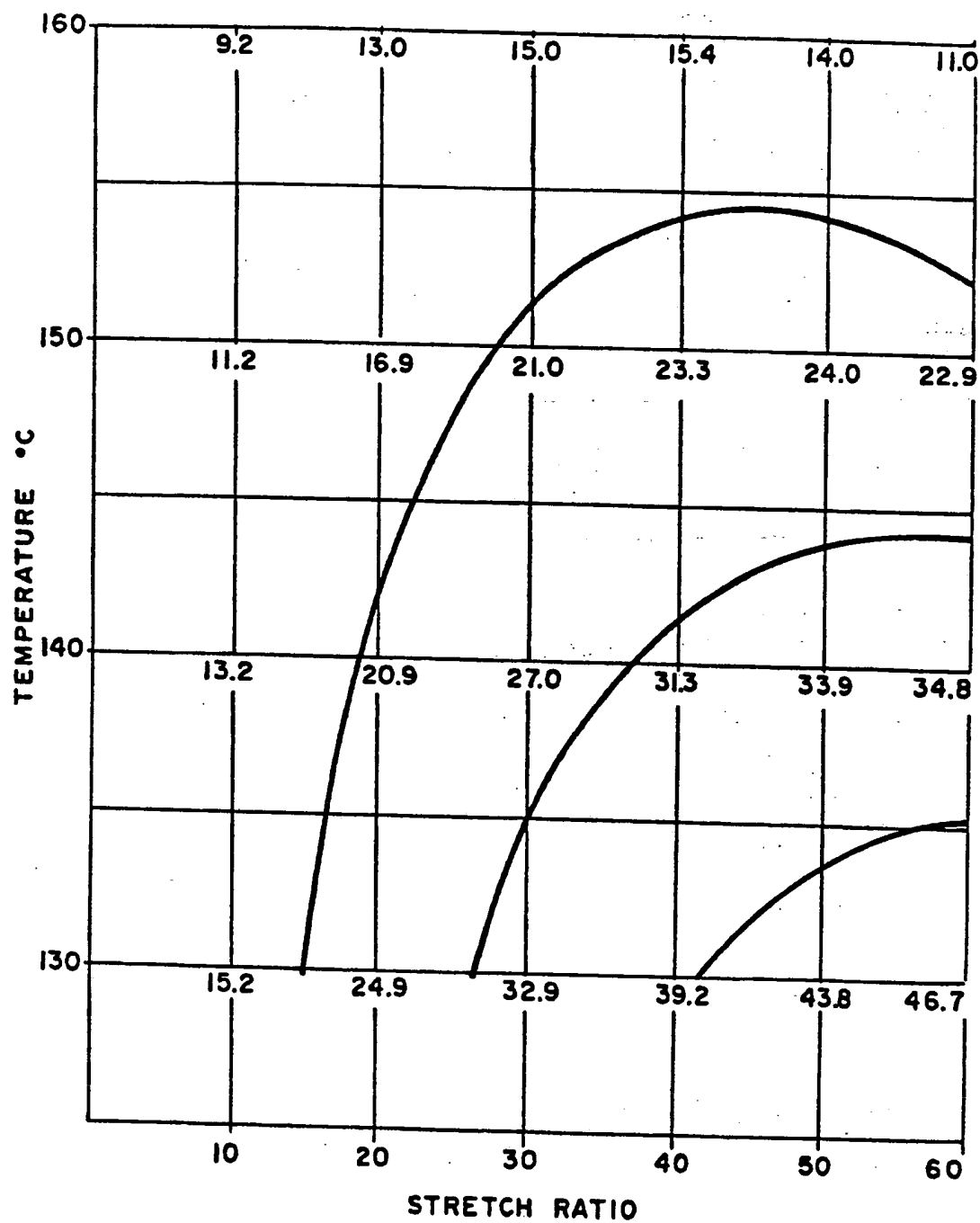point less than 50°C.

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FIG. 1

FIG. 2

140°C = STRETCH TEMP.

24 IV PE

FIG. 3

4% GEL CONCENTRATION
24 IV

FIG. 4

FIG. 5

F I G. 6

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FIG. 7

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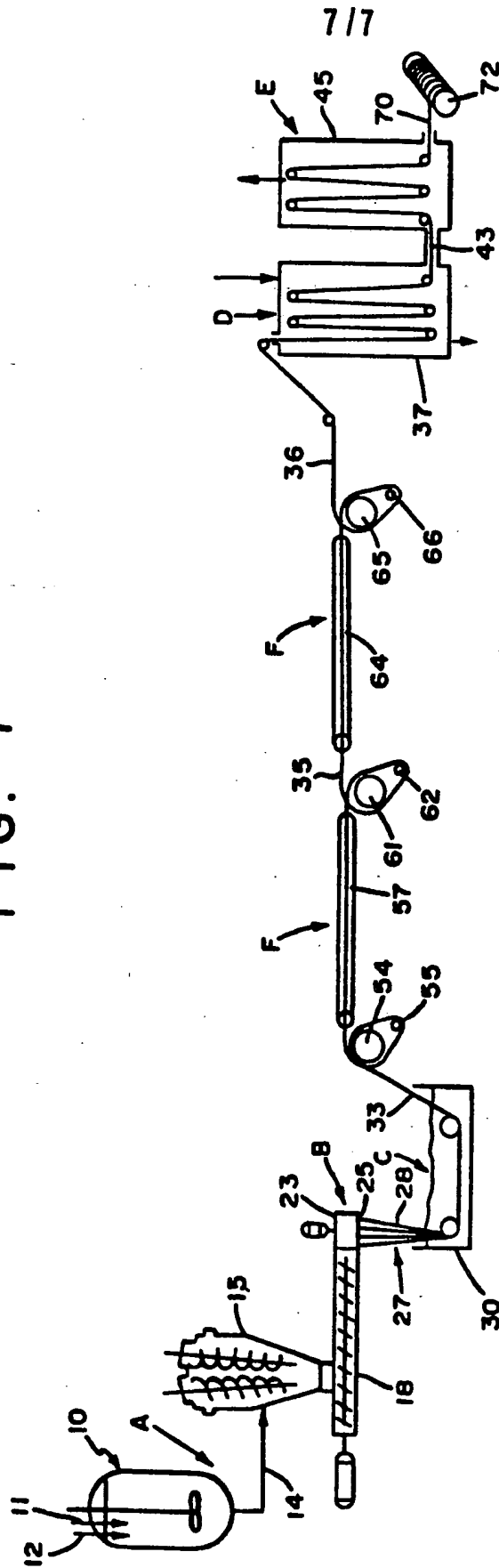**EUROPEAN SEARCH REPORT**

Application number

EP 82 10 2964
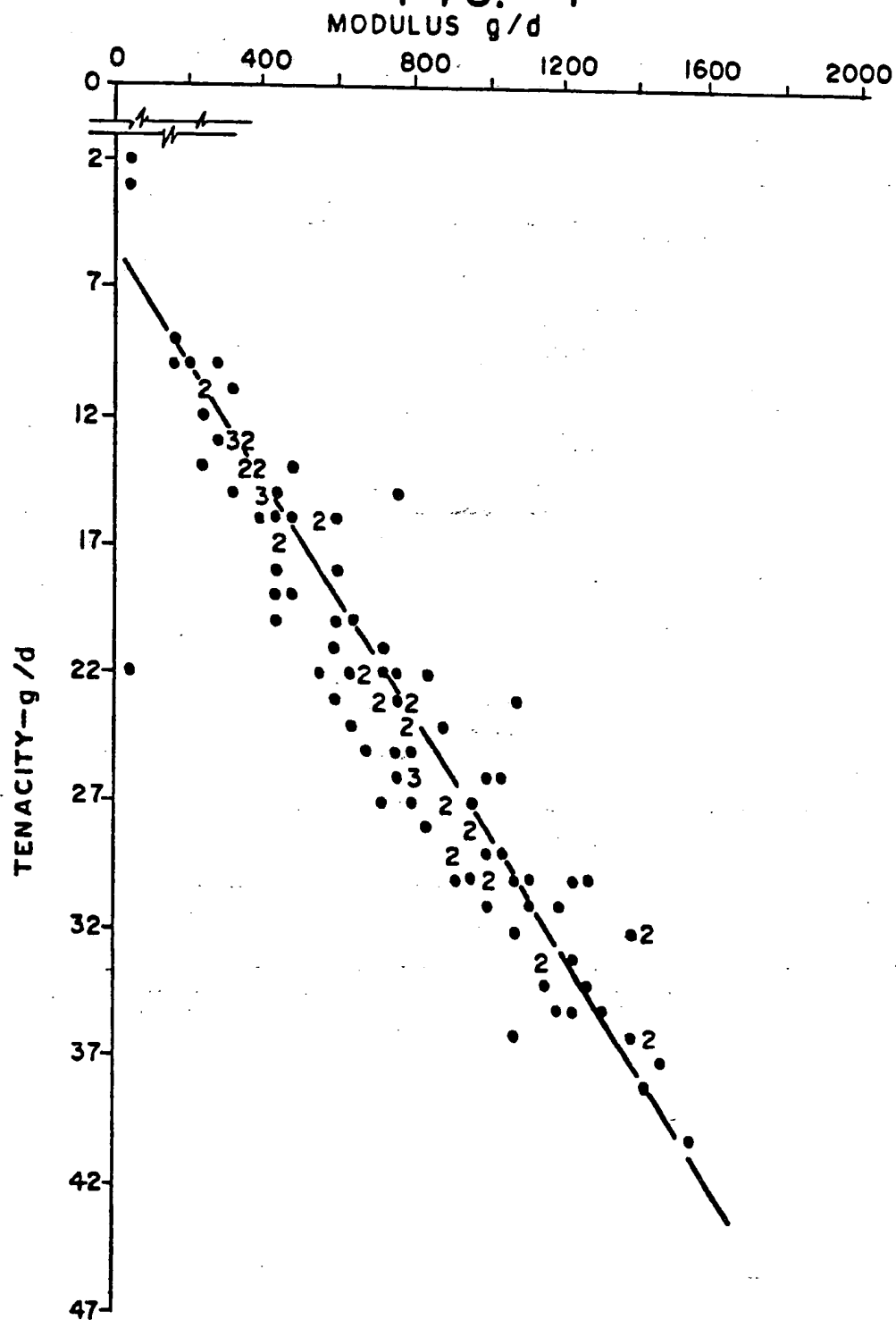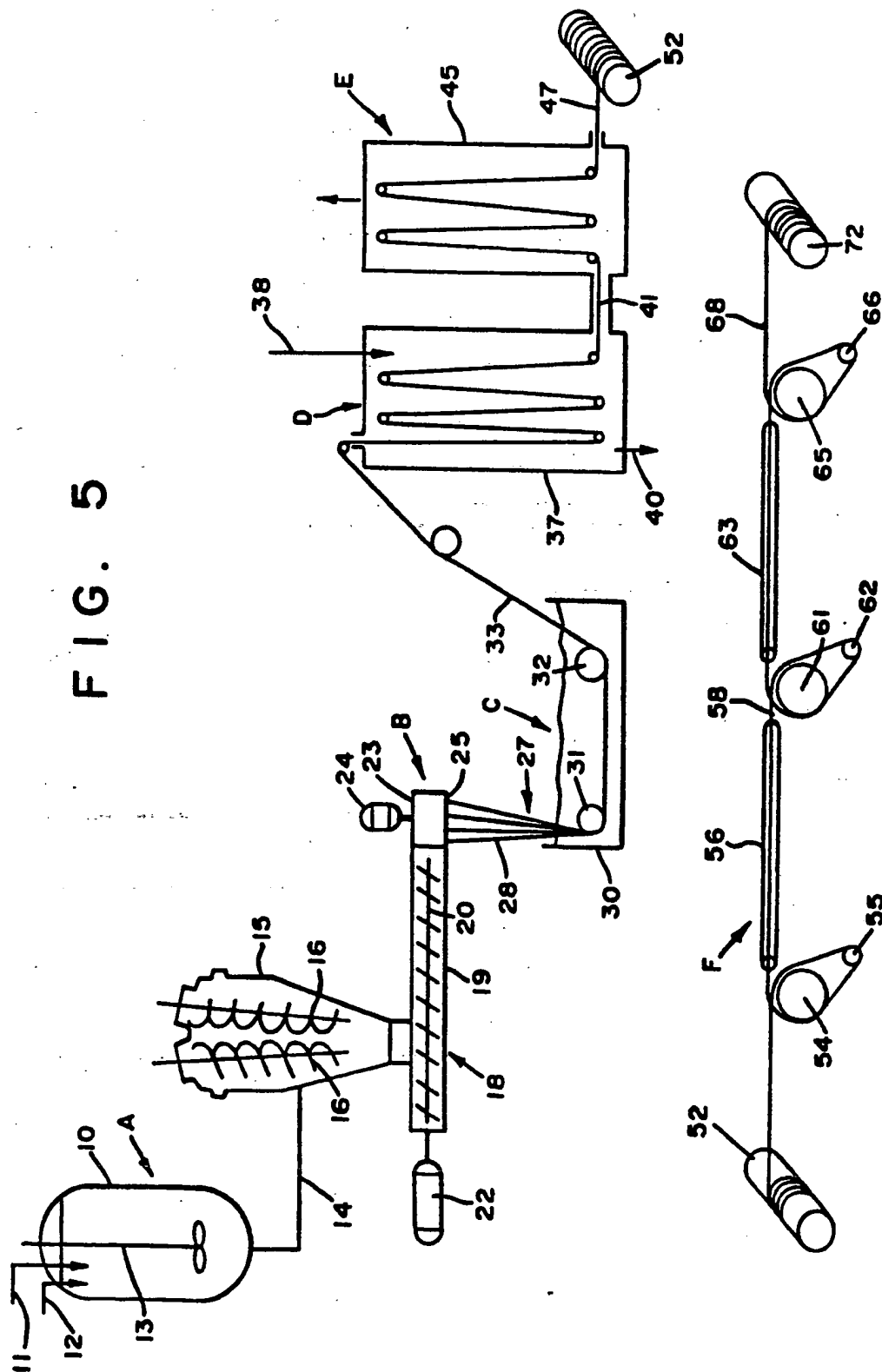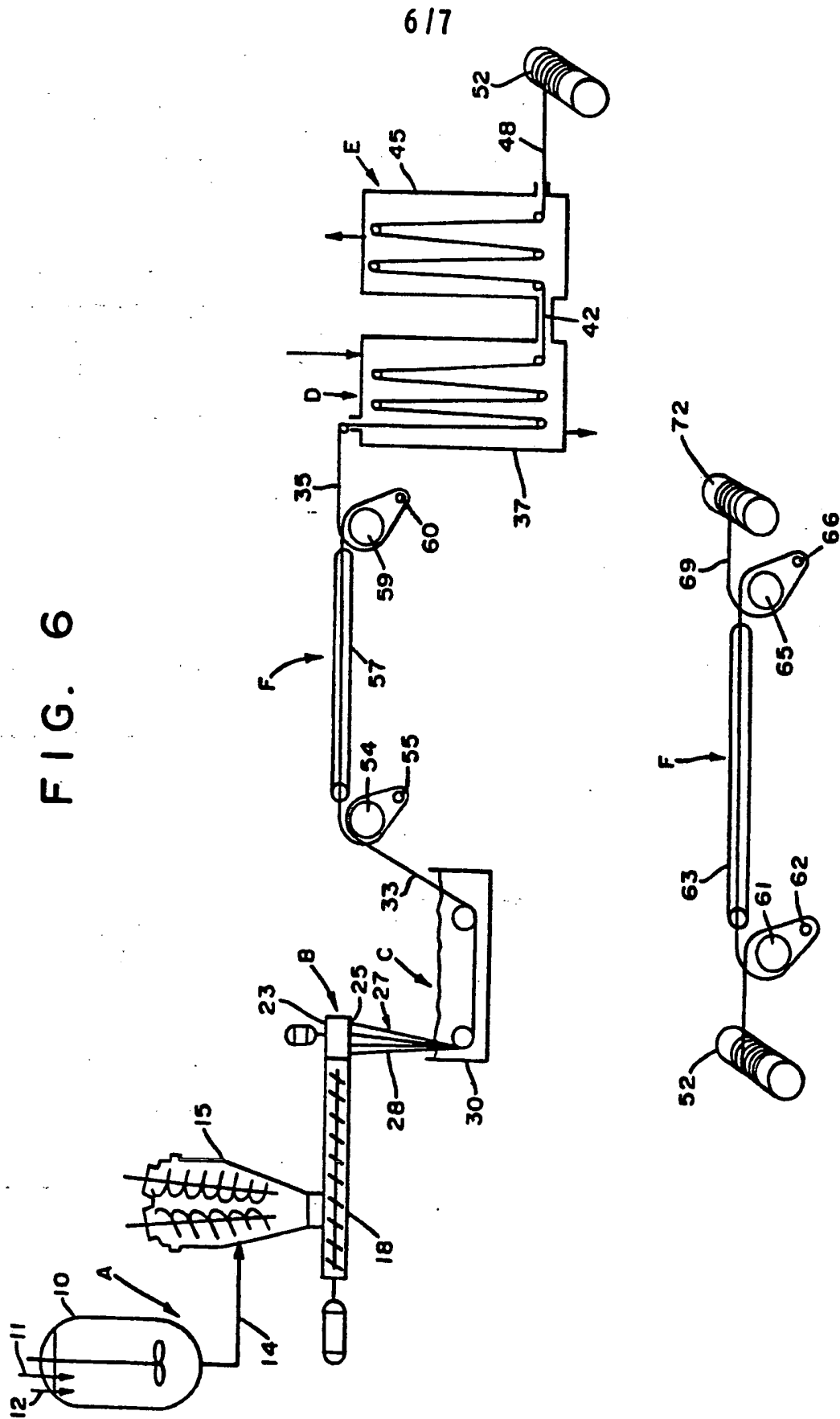
DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,A	GB-A-2 051 667 (STAMICARBON)		D 01 F 6/04

D,A	GB-A-2 042 414 (STAMICARBON) & DE - A - 3 004 699		

D,A	POLYMER BULLETIN, vol.1, 1979, Springer Verlag, Berlin (DE) B. KALB et al.: "Spinning of high molecular weight polyethylene solution and subsequent drawing in a temperature gradient", pages 871-876		

D,A	POLYMER BULLETIN, vol.2, 1980, Springer Verlag, Berlin (DE) J. SMOOK et al.: "Influence of spinning/hot drawing conditions on the tensile strength of porous high molecular weight polyethylene", pages 775-783		TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
	-----		D 01 F D 01 D

The present search report has been drawn up for all claims

Place of search THE HAGUE	Date of completion of the search 01-07-1982	Examiner VAN GOETHEM G.A.J.M.